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19. ABSTRACT (Continue on reverse if necessary and identify by block number) This program dealt with the development and application of new approaches for producing and evaluating semi-empirical (lumped parameter) models of physical processes. Procedures using local sensitivity gradient methods were used to study the existing lumped kinetic models for the moist carbon monoxide oxidation to show that transport processes can cause oversimplified lumped models derived from homogeneous kinetics to fail when applied to flame propagation systems. New models are under development which will include the appropriate level of detail. A Lie group formalism was developed to address global parameter space mapping issues for first order differential equations.					
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Introduction

The design and optimization of realistic engineering combustion devices involves the construction and execution of complex mathematical models. These models will typically involve combustion kinetics as well as transport processes with the physics and chemistry described by many parameters which are imprecisely known. In addition, existing freedom for choosing combustion chamber design will introduce other potentially controllable parameters into the model. Therefore, a central problem in all design problems concerns an understanding of system performance with respect to its parameter values. Except for the simplest models, such an understanding will necessitate extensive computer calculations, and repeated execution for each new set of parameters will lead to prohibitive expense. The goal of this program is to provide new insights as to how to simplify detailed submodels which cause the overall system calculations to be prohibitively difficult, and to exercise the techniques to develop simplified chemical kinetic models which provide sufficient detail for generating accurate modeling results.

Work Statement

The work statement for this program is as follows:

1. Model systems will be studied to establish the use of elementary sensitivity coefficients, Green's function elements and derived sensitivity coefficients for lumping purposes. Appropriate numerical procedures will be employed including eigenvector-eigenvalue analysis and rank reduction of the appropriate sensitivity matrices.
2. The sensitivity techniques of item 1 will be developed with carbon monoxide/hydrogen/oxygen combustion as a test case for systematic model reduction and lumping. The ensuing lumped models will be compared with those existing in the literature for their predictive capabilities.
3. Lie algebra techniques for parameter space mapping and control will be developed starting with temporal systems. Special attention will be given to using the techniques for performing finite excursions through parameter space. As the tools develop, they will applied to the lumping consideration above, as well as to design and control problems relevant to combustion systems.
4. Appropriate advanced development are planned to extend the analysis procedures to more complex combustion chemistry and to include both spatial and temporal calculation comparisons of lumped and detailed models.



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Status of Research

A portion of the program is devoted to applying advanced, local sensitivity analysis and modeling techniques to comprehensive, elementary reaction mechanisms to aid in the development of such lumped kinetic models. The chemical systems of current interest are the $H_2/O_2/N_2$ and the $CO_2/H_2O/O_2/N_2$ reactions with and without the oxides of nitrogen chemistry. During the past year, this work concentrated on studying existing lumped kinetic models in order to clearly define and document their inadequacies and the reasons for these deficiencies. In addition, studies were initiated to determine the "lumpability" (i.e., the achievable degree of reduction) of the chemical systems of interest. Along these lines, work is proceeding towards the development of new lumped parameter models. Details of this work are described briefly below, and in more detail, in the attached manuscripts which have been submitted for review.

Existing lumped parameter models have been analyzed by comparing the predictions of these reduced models with those of validated, elementary reaction models. Furthermore, the original semi-empirical parameters were re-evaluated from the data generated from the detailed calculations. This is in contrast to the traditional evaluation of these parameters via fitting the empirical models to measured experimental data. The results of these studies generally showed existing models to be valid, but only within the limited ranges of environmental conditions over which they were originally calibrated. Hence, one may conclude that it is crucial that any newly developed lumped parameter model be validated over the entire range of environmental conditions of interest to the specific application. More importantly, lumped parameter models valid for one type of physical problem were generally found not valid for another problem. For example, a model constructed from a purely chemical system is not extendable to one with transport. Although these early conclusions might at first glance give a bleak picture to the outcome of the proposed work (in that any lumped parameter model developed will be problem and condition specific), the results of gradient sensitivity analyses have revealed a more encouraging outlook.

Gradient sensitivity analysis has been applied separately to both detailed elementary models and to lumped parameter models and simultaneously to both types of models in order to analyze for correlations between parameters from each type of model. The results from these studies have rigorously shown, as a function of the environmental conditions, that changes in the values of lumped parameters could be directly correlated to changes in the underlying structure of the elementary reaction mechanism. Furthermore, these results indicated that to accommodate for the changes in the elementary reaction mechanism structure, both the lumped model parameters and the governing lumping equations must be reformulated.

Examinations of the Green's function response gradients and the first order elementary gradients showed striking similarities in their profiles. These similarities occur for a number of reasons and generally indicate coupled dependencies among the variables of the system. For example, the Green's function coefficients of the $\text{CO}/\text{H}_2\text{O}/\text{O}_2$ reaction showed similar response surfaces for all intermediates in temporal problems. This particular observed similarity was a result of the steady state coupling among all intermediates. From a model reduction standpoint, these types of couplings can be used to evaluate the degree of system reduction.

Current research is investigating systematic procedures to determine the maximum degree of reduction in the system to maintain the accuracy of selected observables. These procedures include eigenvalue - eigenvector analysis and rank reduction of the gradient matrices described above.

Over the past year progress has also been made on three other projects all in general areas relating to the mathematics of kinetic system reduction and model analysis. These efforts are of potentially broad relevance in combustion and related kinetic phenomena.

I. The Rigorous Criteria for the Lumping of Kinetic Systems

The lumping of kinetic systems has been traditionally approached by judiciously applying kinetic insights to reduce kinetic models. Remarkable progress has been achieved by this simple means, but it is clear that a more rigorous and systematic approach is necessary. As a first step in this direction we have presented the necessary characteristics to be satisfied by a coupled set of kinetic equations in order for them to admit to lumping or system reduction. The criteria extend previous work along these lines which was restricted to only linear kinetic systems. A set of theorems has been established to test whether a system is rigorously lumpable based on the form of the chemical mechanism or more explicitly, the Jacobian of the set of kinetic equations. The lumping is defined by achieving a reduced number of chemical species which are in general expressed as a linear combination of the original set. As a result of the theorems and analysis it is possible to establish the form of this linear transformation generating the lumping process. Although realistic kinetic systems will not likely admit to exact lumping, the significance of this work resides in the fact that we have a basis upon which to build approximate lumping schemes utilizing knowledge of the exact criteria for lumpability. Approximate lumping schemes based on these notions are currently being developed as a continuation of this project.

II. Lie Generators for the Parameter Space Mapping of Kinetic Systems

The practical understanding of any kinetic system requires detailed knowledge about its parameter space which is spanned by the system rate constants and initial chemical species concentrations. In some cases, these parameters may be controlled in the laboratory and in other situations knowledge of the kinetic system behavior in the space is sought for a more thorough understanding of the kinetic processes. Research is continuing on the establishment of a set of Lie generators capable of mapping solutions to the kinetic equations throughout this parameter space. In our previous work we had already established the differential equations determining the generator accomplishing this task and had illustrated it for linear kinetic systems. As a natural extension of this work we have now treated nonlinear systems through second order kinetics. In particular we have shown that it is possible under certain conditions to map from first to second order kinetics and visa versa. As a simple illustration of these techniques, two coupled kinetic equations exhibiting competing chemical processes have been studied and the explicit time independent Lie generators established. The use of symbolic computation has been quite helpful and will be especially important for more complex problems. In the future, this work will be extended to include the possibility of constraints on the system parameters and this situation is especially important for control or optimization applications of the technique.

III. The Practical Factorization of Kinetic System Evolution Operators

The critical step in both solving a set of kinetic equations as well as analyzing its parametric properties using Lie group techniques involves the calculation and analysis of the evolution operator of the physical system. Knowledge of this operator essentially provides a complete description of the system solution and traditional methods based on direct numerical integration of the equations do not lead to the necessary analytical structure, particularly important when seeking physical insight. In this work we have established a new method to factorize the evolution operators into an infinite product of simple evolution operators. The method uses Lie operator algebra and the evolution operators take on an exponential form. The method has broad applications including to the areas of sensitivity analysis and the solution of kinetic equations. A sequence of approximants to the evolution operator may be generated and under certain conditions the convergence of these approximants is remarkably high. This work considered the general formulation of the scheme as well as its convergence properties. Research is continuing on further development of the procedure as well as applications to nonlinear kinetic systems.

Cumulative Chronological List of Publications

R. Yetter, F.L. Dryer and H. Rabitz, "Correlations Between Parameters of Global and Elementary Chemical Kinetic Mechanisms", ABSTRACT, Eastern States Sectional Meeting of the Combustion Institute, Phila., PA, Nov. 4-6, 1985.

L. Hubbard, C. Wulfman, and H. Rabitz, "Parameter space Mapping of First Order Linear Ordinary Differential Equations" J. Phys. Chem, 90, 2273 (1986).

R.A. Yetter, F.L. Dryer, and H. Rabitz, "Complications of One Step Kinetics for Moist CO Oxidation", Twenty-First International Symposium on Combustion, The Combustion Institute, Pittsburgh, PA, To be Published in Proceedings, 1987.

S. Shi and H. Rabitz, "Functional Transformations and Their Application in Study of Group Properties of Integro-Differential Equations and Ordinary Differential Equations", J. Mathematics and Physics, in review, 1986.

M. Demiralp and H. Rabitz, "Factorization of Certain Evolution Operators using Lie Algebra: Formulation of the Method", J. Mathematics and Physics, in review, 1986.

Presentations

R. Yetter, F.L. Dryer and H. Rabitz, "Correlations Between Parameters of Global and Elementary Chemical Kinetic Mechanisms", ABSTRACT, presented at the Eastern States Sectional Meeting of the Combustion Institute, Phila., PA, Nov. 4-6, 1985.

R.A. Yetter, F.L. Dryer, and H. Rabitz, "Complications of One Step Kinetics for Moist CO Oxidation", presented at the Twenty-First International Symposium on Combustion, August 20-25, Munnich West Germany.

H. Rabitz, "Lasers, Molecules and Methods", Los Alamos, July, 1986.

H. Rabitz, Univeristy of the Pacific, March, 1986.

H. Rabitz, Stanford University, March, 1986.

H. Rabitz, California Institute of Technology, March, 1986.

H. Rabitz, University of California, Santa Barbara, March, 1986.

H. Rabitz, Lawrence Livermore Laboratories, March, 1986.

H. Rabitz, Univeristy of California, Los Angeles, March, 1986.

H. Rabitz, Conference on Mathematical Programming with Data Perturbations, Washington, DC, May, 1986.

H. Rabitz, University of Iowa, May, 1986.

H. Rabitz, NASA Conference on Sensitivity Methods in Engineering
Hampton, Virginia, September, 1986.

H. Rabitz, Chevron Research, June, 1986.

H. Rabitz, The Aerospace Corporation, June, 1986.

H. Rabitz, NASA/Ames Laboratories, May, 1986.

H. Rabitz, The University of Indiana, October, 1986.

Vitae

DR. FREDERICK L. DRYER

PROFESSOR
UNDERGRADUATE DEPARTMENTAL REPRESENTATIVE
PRINCETON UNIVERSITY

Dr. Frederick L. Dryer received his Bachelor of Engineering Degree in Aeronautical Engineering from Rensselaer Polytechnic Institute, Troy, New York in 1966 and a Phd. degree in Aerospace and Mechanical Sciences from Princeton University, Princeton, New Jersey in 1972. After serving on the Professional Research Staff in the Mechanical and Aerospace Engineering Department of Princeton University for eight years, he joined the academic faculty of the department as a tenured Associate Professor in 1981. Dr. Dryer was on sabbatical leave during the 1982-83 academic year as a private consultant to industry, and he returned to the University in July 1983 as a Full Professor in the Mechanical and Aerospace Engineering Department. Dr. Dryer has served as Undergraduate Departmental Representative since November of 1984.

Dr. Dryer's principal research interests are in the fundamental combustion sciences with particular emphasis in high temperature combustion chemistry, formation/ignition/secondary atomization/liquid phase chemistry of fuel droplets, and fire-safety-related properties of conventional and synthetic fuels. In collaboration with Professor Irvin Glassman (Princeton University), he developed and maintains a Fuels Research Group typically consisting of seven professionals and ten graduate students, and occupying about 3500 square feet of laboratory space. Research efforts are supported by grants and/or contracts from government, private foundations and industry.

Dr. Dryer has published over seventy-five technical articles, lectured, and consulted extensively on the above as well as other combustion and energy-related subjects. He has contributed invited presentations on two separate occasions to the International Symposiums of the Combustion Institute (1976, 1981) and on numerous other occasions to the regional, national, or international meetings of other organizations including the American Chemical Society, AGARD/NATO, American Institute of Aeronautics and Astronautics, American Physical Society, Eastern, Central, and Western Sectional Meetings of the Combustion Institute, National Bureau of Standards, U.S. Army Research Office, and National Aeronautics and Space Administration. In 1979-80, he served on technical panels and committees for the National Academy of Sciences in assessing automotive emission characteristics and hazards from both catalytically-controlled spark ignition and diesel light vehicles.

Dr. Dryer served as Associate Editor of the international journal, Combustion Science and Technology, from 1977-1986 and is presently a member of the editorial board. He is a member of Tau Beta Pi, Sigma Gamma Tau, and Sigma Xi Engineering Honoraries, The Combustion Institute, The American Chemical Society, and The American Society of Mechanical Engineers.

DR. R.A. YETTER

PROFESSIONAL RESEARCH STAFF
FUELS RESEARCH LABORATORY

Dr. Yetter holds four degrees in Mechanical Engineering; a Bachelor of Science degree from Syracuse University (1974), a Master of Science degree from Cornell University (1980), a Master of Arts degree from Princeton University, and a Doctor of Philosophy degree from Princeton University (1985).

Dr. Yetter has both industrial and laboratory experience as a Research Engineer with the Chemical Sciences Laboratory, Fuels and Lubricants Department, of the Ford Motor Company (3 years) and as a Research Assistant with the Combustion Sciences Laboratory, Department of Energy and Environmental Science, of the Brookhaven National Laboratory (1/2 year). He is currently a Research Collaborator for the Department of Applied Science at the Brookhaven National Laboratory. In July 1985, he joined the Professional Research Staff in the Fuels Research Laboratory.


Dr. Yetter's principal research interest is in the combustion science field with current emphasis in high temperature combustion chemistry, flame structure, and sensitivity analysis theory. He has devoted his work equally among experimental and theoretical studies particularly emphasizing the integration of these two efforts.

Dr. Yetter has been a reviewer for major journals in the field of combustion, and has presented a number of papers at both national and international scientific meetings. He is also an author of several scientific publications.

Herschel Rabitz

Personal and Professional Vita

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Education: B.S. in Chemistry, University of California
Berkeley, 1966

Ph.D in Chemical Physics, Harvard
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Postdoctoral Associate, University of Wisconsin,
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Academic Experience: Assistant Professor of Chemistry, Princeton University
1971-1976

Associate Professor of Chemistry, Princeton University
1976-1980

Professor of Chemistry, Princeton University, 1980-

Applied Mathematics Program, Princeton University,
Affiliated Member and Acting Director, 1984

Societies: American Physical Society
American Association for the Advancement of Science
American Chemical Society
Sigma Xi
Phi Beta Kappa

Honors: Camille and Henry Dreyfus Teacher-Scholar, 1974-1979
Alfred P. Sloan Fellow, 1975-1979

**Nonacademic
Activities:** Chairman, Princeton Section of the American Chemical
Society, 1977-1978

Associate Chairman, Gordon Conference on Few Body
Problems in Chemistry and Physics, 1981

Chairman, Gordon Conference, Dynamics of Simple
Systems in Chemistry and Physics, 1984

Dr. Lynn Hubbard, Research Associate

Dr. Lynn Hubbard attained her Ph.D. in physical chemistry from the University of California, Riverside in 1980. As a postdoctoral fellow, Dr. Hubbard worked with Professor William Miller at Berkeley from June 1980 until October 1983, when she came to Princeton to join Professor Rabitz' research group. Dr. Hubbard's thesis research primarily involved the application of molecular orbital theory and semiclassical molecular dynamics to investigations of the primary photochemical event in rhodopsin, dimutation of superoxide by superoxide dimutase, and the photochemistry and excited state geometries of acetaldehyde and the visual chromophores. Other research interests include: atmospheric modelling; biologically oriented electronic structure calculations; and gas-surface interactions and related chemical/physical processes. While at Princeton, Dr. Hubbard conducted research on Lie group techniques for parameter space mapping in chemical kinetics problems.

Dr. Shenghua Shi, Research Associate

Dr. Shenghua Shi was trained as an engineer in the Peoples Republic of China and in 1984 attained his Ph.D. in chemical physics from the University of California, Berkeley, under the direction of Professor William Miller. His thesis research concerned quantum mechanical and semiclassical approaches to molecular dynamics. He joined Professor Rabitz' research group in November, 1984. Other research interests include functional Lie group techniques for the solution and analysis of physically important differential equations, the study of intramolecular energy transfer in complex polyatomic molecules; and application of control theory ideas to the design of optical pumping experiments to ultimately control chemical processes.

Dr. Metin Demiralp, Visiting Research Staff

Dr. Demiralp received his M.S. in chemical engineering in 1971 and his Ph.D. in physical chemistry in 1975 from the University of Istanbul, Turkey. From 1970 to 1978 he was affiliated at various levels with the Marmara Research Institute in Turkey, Applied Mathematics Department. He came to Princeton for a year as a research associate in Professor Rabitz' group and then joined the Research Institute of Basic Sciences in Turkey, Applied Mathematics Department. During the summers of 1985 and 1986, he once again returned to Princeton as Visiting Research Staff. His research interests include applied mathematics; quantum mechanics; differential equations; linear operators; quantum chemistry; evolution operators (classical and quantum mechanical cases); algebraic methods of eigenvalue problems; and resolvent techniques.

Professor Carl Wulfman

Professor Wulfman received his B.S. in chemistry and math from the University of Michigan in 1953 and attained his Ph.D. from the University of London in 1957. His thesis research involved theoretical organic chemistry. In 1961, he came to the University of the Pacific, Stockton as Chairman of the Pysics Department where he is currently a Professor of Physics. During the fall of 1983, he came to Princeton as a Visiting Fellow to work with Professor Rabitz. Research interests include group analysis of differential equations, physics and chemistry; molecular physics and atomic physics.

FACTORIZATION OF CERTAIN EVOLUTION OPERATORS
USING LIE ALGEBRA: FORMULATION OF THE METHOD

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Abstract

In this work a new method to factorize certain evolution operators into an infinite product of simple evolution operators is presented. The method uses Lie operator algebra and the evolution operators are restricted to exponential form. The argument of these forms is a first order linear partial differential operator. The method has broad applications including to the areas of sensitivity analysis, the solution of ordinary differential equations and the solution of Liouville's equation. A sequence of ξ -approximants are generated to represent the Lie operators. Under certain conditions the convergence rate of the ξ -approximant sequences is remarkably high. This work only presents the general formulation of the scheme and some simple illustrative examples. Investigation of convergence properties is given in a companion paper.

I. Introduction

A system with n -degrees of freedom may be characterized by n variables, x_1, \dots, x_n . The real Euclidean space of these variables is called the phase space of the system. If any two points in the phase space are related by a unique transformation whose functional structure does not depend on the location of the points, then one can define an evolution operator for the system. In mathematical form this can be expressed as

$$x_f = Q(x_i) \quad (I.1)$$

where x_i and x_f represent the initial and final point, respectively. Since any two points of an n -dimensional phase space may be connected by a continuous curve, it is possible to use a tracing parameter which defines the position of the system on this curve during its evolution from its initial state x_i to its final state x_f . This circumstance often arises where time is the evolutionary parameter and we will accordingly denote the parameter as t . Therefore, the initial and final states of the system can be characterized by the scalar instants of time t_i and t_f . Hence the evolution operator Q can be represented as $Q(t_f, t_i)$ and

$$x_f = Q(t_f, t_i) \cdot x_i \quad (I.2)$$

where the dot is used to symbolically represent the effect of Q on x_i , which is generally nonlinear in character. In many applications one can find practical expressions for the operator Q if t_i and t_f are sufficiently close to each other. Hence,

the global evolution operator $Q(t_f, t_i)$ may be factorized into a simple sequence of evolutionary steps

$$Q(t_f, t_i) = Q(t_f, t_m) \cdot Q(t_m, t_{m-1}) \dots Q(t_1, t_i) \quad (I.3)$$

and by choosing m sufficiently large this factorization can characterize the global evolution of the system. If the simple short time interval solutions were exactly calculable, then the number of such evolutions, m , would lose its importance. However, in reality, even the simple evolutions can often be only approximately determined. In such a case, the number of increments m is significant since errors can accumulate to possibly create numerical instabilities. In addition, the factorization requires operators at times other than the initial and final specified values. Therefore, a more global factorization of the evolution operator such as suggested in this paper would be more attractive.

The present work considers the factorization of the evolution operator into a sequence of simple global evolution operators. The scheme presented will maintain its validity only on a special subclass of evolution operators. First, we restrict the system under consideration to being autonomous such that the evolution operator has the following simple structure

$$Q(t_f, t_i) = Q(t_f - t_i) \quad (I.4)$$

In general, the complete class of all evolution operators is a union of non-autonomous and autonomous evolutionary operators. We also restrict ourselves to autonomous evolution operators having an exponential form

$$Q(t_f - t_i) = e^{(t_f - t_i)S} \quad (I.5)$$

where S denotes a time-independent operator. The class of exponential operators can be divided further into subclasses by specifying the nature of the operator S . Among these subclasses, the quantum mechanical exponential operators can be defined as follows

$$S = -i\hat{H}$$

where dimensionless quantities are used and \hat{H} denotes the Hamiltonian of the system under consideration. Unless \hat{H} has special structure, the global factorization of this type of evolution operator using Lie operator algebra is not possible due to the fact that \hat{H} is generally a second order partial differential operator which will not form a closed finite group under commutation operations. This difficulty can nevertheless be circumvented for Hamiltonian systems by consideration of the Liouville operator. This latter operator is amongst the classes considered below.

An important class of evolution operators is included in the following definition

$$S = L = \sum_{j=1}^N f_j(x_1, \dots, x_N) \frac{\partial}{\partial x_j} \quad (I.6)$$

where the dimension or number of degrees of freedom of the system may be finite or infinite. The finite dimensional case may be directly related to the corresponding initial value problem produced by the set of ordinary differential equations¹,

$\dot{x}_j = f_j(x_1, x_2, \dots, x_N)$. Since almost every partial differential

equation with initial conditions can be cast into an infinite set of ordinary differential equations through an appropriately chosen basis set expansion, we may consider the Lie operator in Eq. (I.6) as capable of treating a wide class of problems. Some caution is still required since the coefficients in Eq. (I.6) are scalars while some formal reductions of partial differential equations to ordinary differential equations can produce matrix coefficients. In summary, we restrict ourselves to operators having the structure of Eq. (I.6) and of finite order N .

Lie operators also arise in other areas besides those mentioned above. For example, the investigation of analytic symplectic maps² and the description of the behavior of trajectories near a reference trajectory for a general Hamiltonian system³ are also other applications. Recent works⁴⁻⁶ have considered the use of Lie transformations to perform parameter space mapping of the solution of ordinary differential equations. Other applications may also be found.

The remainder of this paper is organized in the following fashion. Section II gives the general formulation of the global factorization for one-dimensional systems followed by a generalization to multi-dimensional systems in Section III. Some illustrative examples are treated in Section IV and concluding remarks are given in Section V.

II. Factorization Procedure in the One-Dimensional Case

Lie exponential evolution operators defined by Eqs. (I.5) and (I.6) frequently arise in many applications. One application that was mentioned above arises in the treatment of ordinary differential equations. In particular, if we can evaluate the effect of the Lie transformation

$$Q = e^{tL} \quad ; \quad L = \underline{f}(\underline{x}) \cdot \underline{\nabla} \quad (\text{II.1})$$

on the position vector \underline{x} around a point \underline{a} in the phase space of a system defined by

$$\dot{\underline{x}} = \underline{f}(\underline{x}) \quad , \quad (\text{II.2})$$

then the solution to these equations may be written as

$$\underline{x}(\underline{a}, t) = [e^{tL} \underline{x}]_{\underline{x}=\underline{a}} \quad (\text{II.3})$$

where $\underline{x}, \underline{a}$ and $\underline{\nabla}$ are defined in the following manner

$$\underline{x}^T = [x_1, x_2, \dots, x_N] \quad (\text{II.4})$$

$$\underline{a}^T = [a_1, a_2, \dots, a_N] \quad (\text{II.5})$$

$$\underline{\nabla}^T = \left[\frac{\partial}{\partial x_1}, \frac{\partial}{\partial x_2}, \dots, \frac{\partial}{\partial x_N} \right] \quad (\text{II.6})$$

This relation between the solution of ordinary differential equations and Lie transformations may conversely be used to determine the action of the operator Q on the position vector by solving the following ordinary differential equation

$$\dot{\underline{\xi}}(\underline{x}, t) = \underline{f}(\underline{\xi}) \quad ; \quad \underline{\xi}(\underline{x}, 0) = \underline{x} \quad (\text{II.7})$$

This approach to determining Q is generally not preferable since Eq. (II.7) is often only soluble by elaborate numerical techniques which will hide the important structure of the desired

transformation. Although the approach pursued here is also approximate, it will still leave the structure of the evolution operator rather apparent.

In order to appreciate the approach taken below, we recall some important properties of Lie transformations

$$e^{tL}[f(x)g(x)] = [e^{tL}f(x)] [e^{tL}g(x)] \quad (\text{II.8})$$

$$e^{tL}f(x) = f(e^{tL}x) \quad (\text{II.9})$$

The first of these equations states that a Lie transformation on a product of two functions $f(x)$, $g(x)$ can be factorized to the product of the Lie transformation on the individual functions. This property is due to the exponential structure of the Lie transformation along with application of the Leibnitz rule of differentiation, and the relation is valid provided that f and g are infinitely differentiable functions. The penetration property in Eq. (II.9) also follows due to the particular structure of the Lie transformation and the assumed infinitely differentiable nature of the function f . Finally, one additional well known property of Lie transformations concerns the special case of the translation operator

$$e^{t\mathbf{a} \cdot \nabla} f(\mathbf{x}) = f(\mathbf{x} + t \mathbf{a}) \quad (\text{II.10})$$

which followed from a simple Taylor expansion of the right hand side.

We now desire to investigate the factorization of Lie transformations for one-dimensional systems. Although the one-dimensional nature of the problem makes it formally rather simple, this case also provides the best means to develop the

factorization scheme presented here. In this case the Lie transformation can be written as

$$Q = \exp\left[tf(x) \frac{\partial}{\partial x}\right] \quad (\text{II.11})$$

where $f(x)$ may have a number of zeros with one assumed to exist at the origin of the complex x -plane. This assumption about the location of a zero of $f(x)$ at the origin does not create any loss of generality since a simple translation can bring one of the zeros of $f(x)$ to the origin. The assumption about the existence of at least one zero of $f(x)$ is more restrictive. However, in problems where $f(x)$ forms the right hand side of an ordinary differential equation, there will usually be at least one stationary point for the solution. Therefore, the assumption about the existence of a zero of the function $f(x)$ may be regarded as a minor loss of generality.

We may now make the additional assumption that the function $f(x)$ may be expanded in a Taylor series

$$f(x) = \sum_{j=1}^{\infty} f_j x^j \quad |x| < \rho \quad (\text{II.12})$$

where the expansion coefficients f_j are taken as known from the definition of the system. The expansion above implies that the system is well characterized, at least in a restrictive domain around the origin of the complex x -plane. We seek the factorization of the evolution operator Q such that every factor has an independent contribution in a fashion analogous to each term in

the Taylor series of Eq. (II.12). To this end we define the flexible factorized structure

$$Q = \exp\left[tf(x)\frac{\partial}{\partial x}\right] = \prod_{j=1}^{\infty} \exp\left[\sigma_j(t)x^j\frac{\partial}{\partial x}\right] \quad (\text{II.13})$$

where $\sigma_j(t)$ are arbitrary at this point and yet to be determined.

Equation (II.13) is the factorization formula for the one-dimensional case.

For the one-dimensional case the factorization in Eq. (II.13) may seem to be unnecessary due to the fact that the equation $\dot{x} = f(x)$ can be solved by the usual techniques of numerical analysis. However, in order to gain insight into the more interesting multi-dimensional case, the present reduced case presents the best way to understand the theory. Despite the existence of some attempts to factorize Q by time ordering techniques with respect to t , to our knowledge there has been no factorization of Q along the lines presented in Eq. (II.13)

Assuming that (II.13) holds and the coefficients σ_j are known, it is a simple matter to determine the effect of the operator Q on x . For this purpose we can investigate the individual effects of the factors in Eq. (II.13)

$$Q^{(j)}x = \exp\left[\sigma_j(t)x^j\frac{\partial}{\partial x}\right] x \quad (\text{II.14})$$

By using a simple variable transformation

$$y = x^{-(j-1)} \quad (\text{II.15})$$

we may write

$$Q^{(j)}x = \exp\left[-(j-1)\sigma_j(t)\frac{\partial}{\partial y}\right] y^{-1/(j-1)} \quad (\text{II.16})$$

and employ the translation operator property of Eq. (II.10) on the y-coordinate

$$Q^{(j)}_x = [y - (j-1)\sigma_j(t)]^{-1/(j-1)} \quad (\text{II.17})$$

or equivalently in terms of the x-coordinate

$$Q^{(j)}_x = \frac{x}{[1 - (j-1)\sigma_j(t)x^{j-1}]^{1/(j-1)}} \quad (\text{II.18})$$

In this formula the positive branch of the root has been taken. This is the fundamental formula of our factorization and it is valid provided the argument of the root appearing in Eq. (II.18) remains positive. We are now able to evaluate the effects of the individual factors in Eq. (II.13). In applications of Eq. (II.13) an approximation to Q would consist of truncating the infinite product involved.

At this point we need to determine the coefficient functions σ_j . To this end we can use the following relation

$$\frac{\partial Q}{\partial t} = \left[\sum_{j=1}^{\infty} f_j x^j \frac{\partial}{\partial x} \right] Q ; Q(0) = I \quad (\text{II.19})$$

which follows from Eqs. (II.12) and (II.13). If we now write

$$Q = Q^{(1)} Q_1 = \exp\left[\sigma_1(t)x \frac{\partial}{\partial x}\right] Q_1 \quad (\text{II.20})$$

we may arrive at

$$\frac{\partial Q_1}{\partial t} = \exp[-\sigma_1(t)x \frac{\partial}{\partial x}] \left[f(x) \frac{\partial}{\partial x} - \dot{\sigma}_1 x \frac{\partial}{\partial x} \right] \exp[\sigma_1(t)x \frac{\partial}{\partial x}] Q_1 \quad (\text{II.21})$$

using the properties in Eqs. (II.8) and (II.9). This result may be re-expressed as

$$\frac{\partial Q_1}{\partial t} = \left\{ \left[\frac{f \left[\exp \left[-\sigma_1 x \frac{\partial}{\partial x} \right] x \right]}{\exp \left[-\sigma_1 x \frac{\partial}{\partial x} \right] x} - \phi_1 \right] x \frac{\partial}{\partial x} \right\} Q_1 \quad (\text{II.22})$$

The following formula

$$\exp \left[-\sigma_1(t) x \frac{\partial}{\partial x} \right] x = \exp(-\sigma_1(t)) \quad (\text{II.23})$$

allows for a rewriting of Eq. (II.22) utilizing the expansion in Eq. (II.12)

$$\frac{\partial Q_1}{\partial t} = \left\{ (f_1 - \phi_1) + (f_2 \exp(-\sigma_1(t)) x) + \dots \right\} x \frac{\partial}{\partial x} Q_1 \quad (\text{II.24})$$

The operator acting on Q_1 on the right hand side of Eq. (II.24) is a power series in x . Each of the terms of this series is independent and in the vicinity of the origin the first term will be dominant. We desire to make Q_1 as slowly varying as possible and therefore demand that the leading term in the series vanish for this purpose

$$\phi_1(t) = f_1 ; \sigma_1(0) = 0 \quad (\text{II.25})$$

The initial condition has been taken as zero to make the simple evolution operator $Q^{(1)}$ unitary. Equation (II.24) now has the form

$$\frac{\partial Q_1}{\partial t} = f^{(1)}(x) x^2 \frac{\partial}{\partial x} Q_1 ; Q_1(0) = I$$

where $f^{(1)}(x)$ can be identified from the remaining series of terms in the brackets of Eq. (II.24) and $f^{(1)}(0)$ is finite. Exactly this same logic may be put forth to evaluate $\sigma_2(t)$ by successively eliminating higher order powers of x in the differential equation. To construct a general recursion we assume knowledge of the first n of the σ_j 's and write

$$Q = \left\{ \prod_{j=1}^n Q^{(j)} \right\} Q_n \quad (\text{II.26})$$

which leads to

$$\frac{\partial Q_n}{\partial t} = f^{(n)}(x) x^{n+1} \frac{\partial}{\partial x} Q_n \quad ; \quad Q_n(0) = I \quad (\text{II.27})$$

The time-dependence of $f^{(n)}(x)$ is not explicitly shown and the function $f^{(n)}(x)$ is regular at the origin of the x -plane. We now may write

$$Q_n = Q^{(n+1)} Q_{n+1} = \exp[\sigma_{n+1}(t) x^{n+1} \frac{\partial}{\partial x}] Q_{n+1} \quad (\text{II.28})$$

and obtain

$$\frac{\partial Q_{n+1}}{\partial t} = \left[f^{(n)} \left[\exp[-\sigma_{n+1}(t) x^{n+1} \frac{\partial}{\partial x}] x \right] - \dot{\sigma}_{n+1} \right] x^{n+1} \frac{\partial}{\partial x} Q_{n+1} \quad (\text{II.29})$$

by utilizing again the properties in Eqs. (II.8) and (II.9). Employing the action of the factorization operator in (II.18) gives

$$\frac{\partial Q_{n+1}}{\partial t} = \left[f^{(n)} \left[\frac{x}{(1+n\sigma_{n+1}(t) x^n)^{1/n}} \right] - \dot{\sigma}_{n+1} \right] x^{n+1} \frac{\partial}{\partial x} Q_{n+1} \quad (\text{II.30})$$

We now apply logic analogous to that leading to Eq. (II.25) and eliminate the dominant contribution to the bracketed quantity multiplying the operator $x^{n+1} \frac{\partial}{\partial x}$ yielding

$$\dot{\sigma}_{n+1} = f^{(n)}(0) \quad ; \quad \sigma_{n+1}(0) = 0 \quad (\text{II.31})$$

where the initial value is again chosen as zero to make $Q^{(n+1)}$ unitary. Therefore we conclude

$$\frac{\partial Q_{n+1}}{\partial t} = f^{(n+1)}(x) x^{n+2} \frac{\partial}{\partial x} Q_{n+1} \quad (\text{II.32})$$

where

$$f^{(n+1)}(x) = \frac{1}{x} \left[f^{(n)} \left[\frac{x}{(1+n\sigma_{n+1}(t) x^n)^{1/n}} \right] - f^{(n)}(0) \right] \quad (\text{II.33})$$

This is a first order recursion relation with the initial condition

$$f^{(1)}(x) = \frac{1}{x^2} [f(\exp(-\sigma_1(t)) x) \exp(\sigma_1(t)) - f_1 x] \quad (\text{II.34})$$

All of the σ -functions can be evaluated analytically in principle, however this is a tedious task and the use of a symbolic programming language such as MACSYMA or REDUCE is recommended. The first five of the σ -functions are given below.

$$\sigma_1(t) = f_1 t \quad (\text{II.35})$$

$$\sigma_2(t) = f_2 g_1(t) \quad (\text{II.36})$$

$$\sigma_3(t) = f_3 g_2(t) \quad (\text{II.37})$$

$$\sigma_4(t) = \left[f_4 + \frac{f_2 f_3}{f_1} \right] g_3(t) - \frac{f_2 f_3}{f_1} g_2(t) \quad (\text{II.38})$$

$$\begin{aligned} \sigma_5(t) = & \left[f_5 + \frac{f_2 f_4}{f_1} + \frac{f_2^2 f_3}{2f_1^2} \right] g_4(t) + \\ & + \left[\frac{f_2 f_4}{f_1} + \frac{f_2^2 f_3}{f_1^2} \right] g_3(t) + \frac{f_2^2 f_3}{2f_1^2} g_2(t) \end{aligned} \quad (\text{II.39})$$

where

$$g_n(t) = \frac{1 - \exp(-nf_1 t)}{nf_1} \quad (\text{II.40})$$

We are now at a point to implement the factorization scheme. The essential approximation is to truncate Eq. (II.13) to a finite order thereby producing the following approximant.

$$\xi_n(x, t) = \left\{ \prod_{j=1}^n Q^{(j)} \right\} x \quad (\text{II.41})$$

If the infinite product representation of Q given by (II.13) converges, then the following result will hold.

$$\xi(x, t) = Qx = \exp \left[tf(x) \frac{\partial}{\partial x} \right] x = \lim_{n \rightarrow \infty} \xi_n \quad (\text{II.42})$$

Since the action of Q on x defines the fundamental operations of concern, we now focus our attention on the ξ -approximants. A recursion relation for these approximants can be obtained by first noting that

$$\xi_{n+1} = \left\{ \prod_{j=1}^n Q^j \right\} \exp \left[\sigma_{n+1}(t) x^{n+1} \frac{\partial}{\partial x} \right] x \quad (\text{II.43})$$

An application of Eq. (II.18) yields

$$\xi_{n+1} = \left\{ \prod_{j=1}^n Q^j \right\} \frac{x}{\left[1 - n \sigma_{n+1} x^n \right]^{\frac{1}{n}}} \quad (\text{II.44})$$

Since a product of Lie transformations is again a Lie transformation, we may use the property in Eq. (II.9) along with Eq. (II.41) to conclude that

$$\xi_{n+1}(x,t) = \frac{\xi_n(x,t)}{\left[1 - n \sigma_{n+1}(t) \xi_n^2(t) \right]^{\frac{1}{n}}} \quad (\text{II.45})$$

This is a rather simple first order recursion (difference equation) whose initial member is evaluated as follows

$$\xi_1(x,t) = \exp \left[\sigma_1(t) x \frac{\partial}{\partial x} \right] x = x \exp(\sigma_1(t)) = x \exp(f_1 t) \quad (\text{II.46})$$

Although this is a simple recursion relation, it is not typically suitable for numerical purposes. Numerical instabilities will occur if f_1 is negative resulting in excessively small quantities for large times t or also under the conditions that x tends to zero. In these cases, error accumulations may occur due to the truncated arithmetic on the computer. To prevent this error we may renormalize the ξ -approximants and define a new recursion relation

$$\xi_{n+1} = \frac{\xi_n}{\left[1 - \bar{\sigma}_{n+1} x^n \xi_n^2 \right]^{\frac{1}{n}}} \quad ; \quad \xi_1 = 1 \quad (\text{II.47})$$

where

$$\bar{\sigma}_{n+1} = n \sigma_{n+1} \exp(n f_1 t) \quad (\text{II.48})$$

The relation between the new approximants and the previous ones is

$$\xi_n(x,t) = \xi_n(x,t) \times \exp(f_1 t) \quad (\text{II.49})$$

which also implies

$$\xi(x,t) = \exp\left[t f(x) \frac{\partial}{\partial x}\right] x = \xi(x,t) \times \exp(f_1 t) \quad (\text{II.50})$$

Since the term $x \exp(f_1 t)$ characterizes the linear response of the system, we can consider $\xi(x,t)$ as a function measuring the deviations of the system from its linear response. We will accordingly refer to ξ as a "deviation function". As can be easily seen, the ξ and ξ -approximants have branch points which move on trajectories in the x -plane. The location of these trajectories determines the convergence regions of the approximants. We shall leave the discussion of this issue and a comparison of the ξ -approximants with Padé approximants to a companion paper.

III. GENERALIZATION OF THE FACTORIZATION SCHEME TO THE MULTIDIMENSIONAL CASE

The logic put forth in section II for a systematic factorization of one dimensional evolution operators may now be generalized to multidimensional cases. In this situation, the evolution operator acting in a space of dimension N has the form

$$Q = \exp(t \underline{f}(\underline{x}) \cdot \underline{\nabla}) \quad (\text{III.1})$$

where

$$\underline{x}^T = [x_1, \dots, x_N] \quad (\text{III.2})$$

$$\underline{\nabla}^T = \left[\frac{\partial}{\partial x_1}, \dots, \frac{\partial}{\partial x_N} \right] \quad (\text{III.3})$$

$$\underline{f}^T = [f_1(\underline{x}), \dots, f_N(\underline{x})] \quad (\text{III.4})$$

The function $\underline{f}(\underline{x})$ is assumed to have a zero at the origin

$$\lim_{|\underline{x}| \rightarrow 0} \underline{f}(\underline{x}) = 0 \quad (\text{III.5})$$

and it is also assumed to be expandable in a multidimensional Taylor series in the variable x_1, \dots, x_N . This latter expansion can be written in tensor form as

$$f_1 = {}^{(1)}f_{1j} x_j + {}^{(2)}f_{1jk} x_j x_k + {}^{(3)}f_{1jkl} x_j x_k x_l + \dots \quad (\text{III.6})$$

where the convention of the explicit summation over repeated indices is used for convenience.

In the one-dimensional case the operator $\exp(\sigma_1 x \frac{\partial}{\partial x})$ played a fundamental role in the first step of establishing a recursion relation for the approximants. The same situation occurs again

here and we shall denote this first degree operator Q_L as taking on the following form

$$Q_L = \exp(\underline{x}^T \underline{\sigma}^{(1)} \underline{\nabla}) \quad (\text{III.7})$$

where $\underline{\sigma}^{(1)}$ is a square matrix or equivalently a second degree tensor. The effect of this operator on the position vector \underline{x} is

$$Q_L \underline{x} = \exp(\underline{\sigma}^{(1)}) \underline{x} \quad (\text{III.8})$$

Since $Q_L \underline{x}$ must be the system linear response we can conclude that

$$\sigma_{jk}^{(1)} = t^{(1)} f_{kj} \quad j, k = 1, \dots, N \quad (\text{III.9})$$

Henceforth, we shall denote the linear response of the system evolution by S ,

$$S = \exp(t^{(1)} \underline{f}) \quad (\text{III.10})$$

Using the definition of the scalar product of two tensors of the same order,

$$A_{j_1 \dots j_n} B_{j_1 \dots j_n} = A \circ B \quad (\text{III.11})$$

we can write the evolution operator in Eq. (III.1) as the infinite order factorized product

$$Q = Q_L \prod_{k=2}^{\infty} \exp[\underline{\sigma}^{(k)} \circ L^{(k)}] \quad (\text{III.12})$$

where $\sigma^{(k)}$ is a k -th order tensor to be determined and $L^{(k)}$ is a tensor valued operator

$$L_{j_1 j_2 \dots j_k}^{(k)} = x_{j_2} x_{j_3} \dots x_{j_k} \frac{\partial}{\partial x_{j_1}} \quad (\text{III.13})$$

The tensor product in the argument of each exponential term in Eq. (III.12) is itself a sum of operators which would be difficult to deal with in practice. Therefore, we have further factorized each individual term in Eq. (III.12) (except Q_L) to obtain

$$Q = Q_L \prod_{k=2}^{\infty} \prod_j^* \exp(\sigma_{j_1 j_2 \dots j_k}^{(k)} L_{j_1 \dots j_k}^{(k)}) \quad (\text{III.14})$$

where it is understood that the coefficient functions $\sigma^{(k)}$ are now distinct from the set in Eq. (III.12). The starred product in this formula means that the product operation is performed over the entire domain of the j -indices. There is no unique ordering to the factorization in Eq. (III.14) for a multi-dimensional case. However, if we define the following operators

$$\bar{Q}^{(n)} = \exp[\sigma^{(n)} \odot L^{(n)}] \quad (\text{III.15})$$

$$Q^{(n)} = \prod_j^* \exp[\sigma_{j_1 j_2 \dots j_n}^{(n)} L_{j_1 \dots j_n}^{(n)}] \quad (\text{III.16})$$

one can prove that

$$\{\bar{Q}^{(n)} x\} - \{Q^{(n)} x\} = O[x^{2n-1}] \quad (\text{III.17})$$

Therefore, within this level of approximation the expressions in Eqs. (III.12) and (III.14) may be considered equivalent. The form given by Eq. (III.14) is practical since each of the sequence of evolution operators acts on a particular coordinate and degree of freedom.

The procedure for determining the σ - tensor is the same as in the previous section, however all scalars, (except time) must be replaced with tensor quantities and the conventional algebra must be replaced with tensor algebra. The details of these operations will not be dealt with further here, but the use of symbolic programming languages would be most helpful in practice. The second degree σ - tensor is given below as an example.

$$\sigma_{jk}^{(2)} = \int_0^t S_{j\mu}(t) {}^{(2)}f_{\mu n_1 n_2} [S^{-1}(t)]_{n_1 k} [S^{-1}(t)]_{n_2 1} dt \quad (III.18)$$

The evaluation of the ξ - approximants can again be accomplished by using the consecutive effects of the individual factors of the evolution operator. Symbolic programming techniques would likely be the best procedure for determining the x_1, \dots, x_N and t dependence of the ξ - approximants.

IV. ILLUSTRATIVE APPLICATIONS

In this section, five problems are considered, each of which exhibits different types of behavior. For the sake of comparison with the techniques introduced in the previous sections, we have chosen analytically soluble problems as described below.

$$1) \quad f(x) = 1 - e^x \quad (IV.1)$$

From traditional linear stability analysis arguments this system is stable for $x > 0$ and unstable for $x < 0$. There is also only one steady state point located at the origin. An analytic expression for the effect of the Lie transformation on x can be written as

$$\xi(x, t) = \exp \left[t f(x) \frac{\partial}{\partial x} \right] x = - \ln \left[1 - (1 - e^{-x}) e^{-t} \right] \quad (IV.2)$$

A careful examination of the structure of $\xi(x, t)$ reveals that its branch point traverses the path from $-\infty$ to $+\infty$ along the horizontal axes $\mp i\pi$ as time evolves. Figure 1a plots the exact deviation function $\xi(x, t)$ and its first five approximants $\xi_n(x, t)$ as defined in Eqs. (II.50) and (II.49) respectively for the case $x=0.1$. It is apparent that the approximants uniformly converge to the true deviation function as n increases. The error between the true deviation function and the $n=5$ approximant is shown in Figure 1b where it is apparent that the error decreases monotonically to an asymptotic value for large times. A similar pair of plots is shown in Figure 2

for $x=5.0$. At this larger value of x qualitatively similar behavior occurs but the rate of convergence of the approximants is slower and the peak in the error function may be a signal of the loss of global convergence. The situation for negative values of x is different as shown in Figure 3. Figure 3 presents the case for $x=-1.0$. The approximants in this case seem to show oscillatory nonmonotonic behavior with regard to true deviation function. The error of each of the approximants is qualitatively similar to that of Figures 1 and 2. At a sufficiently large negative value of x singular behavior shows up resulting in apparent non-convergence.

$$11) \quad f(x) = 1 - e^{-x} \quad (\text{IV.3})$$

This system is unstable for positive x values due to the first Taylor coefficient being positive. It has only one steady state point located at the origin of the x -plane. The analytic expression of the Lie transformation effect on x is

$$\xi(x,t) = \ln\{1+(e^x-1)e^t\} \quad (\text{IV.4})$$

The branch point trajectory of this system matches with the negative portion of the real axis of the x -plane. The branch point moves on this line towards the origin as time evolves and reaches there in the limit that $t \rightarrow \infty$. Figure 4 shows the deviation approximants and the error of the fifth member for $x=0.1$. Apparent convergence failure is observed, however during a finite time interval starting from $t=0$ there is temporary convergence.

$$(111) \quad f(x) = \sin x$$

(IV.5)

This system is unstable around $x=0$ for $x>0$, however it has infinitely many steady state points and they alternatively make the system either stable or unstable. Figures 5 depicts the approximant behavior for the case $x=1.0$. There is apparent convergence behavior in the figure, however a peak in the error function may again be a signal of the loss of global convergence. It is difficult to prove this point from only a finite number of approximants. An additional calculation is shown in Figure 6 for $x = 5.0$ which is beyond the second stationary point of $\sin x$. This well behaved nature of the approximants is probably due to the fact that all the branch points of this system are purely imaginary.

(v) Stakgold problem⁷

This problem is associated with the consideration of two coupled nonlinear differential equations with system coefficients given by

$$\begin{aligned} f_1(x_1, x_2) &= \lambda x_1 - x_2 - x_1(x_1^2 + x_2^2) \\ f_2(x_1, x_2) &= \lambda x_2 - x_1 - x_2(x_1^2 + x_2^2) \end{aligned} \quad (\text{IV.6})$$

The analytic expression for the effect of the Lie transformation on the position vector is

$$\begin{aligned} \xi_1(t) &= (x_1 \cos t - x_2 \sin t) e^{-|\lambda|t} \eta(\underline{x}, t) \\ \xi_2(t) &= (x_1 \sin t + x_2 \cos t) e^{-|\lambda|t} \eta(\underline{x}, t) \end{aligned} \quad (\text{IV.7})$$

where λ is assumed to be negative and η is defined as follows

$$\eta(\underline{x}, t) = \left[1 + \frac{x_1^2 + x_2^2}{|\lambda|} \left[1 - e^{-2|\lambda|t} \right] \right]^{-\frac{1}{2}} \quad (\text{IV.8})$$

This system is stable as long as λ remains negative. In the case of positive λ the same condition again holds but the system does not have a steady state solution and a limit cycle appears.

In applying the method of Section III to Eq. (IV.6) we will find that the system has only the following non zero tensor coefficients

$$\begin{aligned} {}^{(1)}f_{11} &= \lambda & {}^{(1)}f_{12} &= -1 \\ {}^{(1)}f_{21} &= 1 & {}^{(1)}f_{22} &= \lambda \end{aligned} \quad (\text{IV.9})$$

$${}^{(3)}f_{1111} = {}^{(3)}f_{1122} = {}^{(3)}f_{2211} = {}^{(3)}f_{2222} = -1 \quad (\text{IV.10})$$

Accordingly, the linear response term would be expressed by the tensor

$$\underline{S} = \exp(t^{(1)} \underline{f}) \quad (\text{IV.11})$$

and elements of this matrix and its inverse are given by the following expressions

$$\begin{aligned} S_{11} &= e^{\lambda t} \cos t & S_{12} &= -e^{\lambda t} \sin t \\ S_{21} &= e^{\lambda t} \sin t & S_{22} &= e^{\lambda t} \cos t \end{aligned} \quad (\text{IV.12})$$

$$\begin{aligned} S_{11}^{(-1)} &= e^{-\lambda t} \cos t & S_{12}^{(-1)} &= e^{-\lambda t} \sin t \\ S_{21}^{(-1)} &= e^{-\lambda t} \sin t & S_{22}^{(-1)} &= e^{-\lambda t} \cos t \end{aligned} \quad (\text{IV.13})$$

Since the second degree Taylor expansion coefficients are zero it follows that

$$\underline{\sigma}^{(2)} = 0 \quad (\text{IV.14})$$

The third order terms are non zero and $\underline{\sigma}^{(3)}$ may be shown as

$$\sigma_{1_1 1_2 1_3 1_4}^{(3)} = \int_0^t S_{1_1 m_1}^{(3)} f_{m_1 m_2 m_3 m_4} S_{m_2 1_2}^{(-1)} S_{m_3 1_3}^{(-1)} S_{m_4 1_4}^{(-1)} dt \quad (\text{IV.15})$$

where the explicit summation rule over repeated indices is employed. After some tedious algebra, one can show that all elements of the $\sigma^{(3)}$ -tensor vanish except for the following four members

$$\begin{aligned} \sigma_{1111}^{(3)}(t) &= \sigma_{1122}^{(3)}(t) = \sigma_{2211}^{(3)}(t) = \\ &= \sigma_{2222}^{(3)}(t) = \frac{e^{-2\lambda t} - 1}{2\lambda} \equiv \sigma_3(t) \end{aligned} \quad (\text{IV.16})$$

This result immediately yields the tensor product

$$\underline{\sigma}^{(3)} \otimes \underline{L}^{(3)} = \sigma_3(t) \left[x_1^2 + x_2^2 \right] \left[x_1 \frac{\partial}{\partial x_1} + x_2 \frac{\partial}{\partial x_2} \right] \quad (\text{IV.17})$$

As can be easily observed the operators $\underline{\sigma}^{(3)} \otimes \underline{L}^{(3)}$ and $\underline{f}^{(3)} \otimes \underline{L}^{(3)}$ commute and therefore there will be no contribution from higher degree terms of the remainder during the elimination of the operator $\underline{\sigma}^{(3)} \otimes \underline{L}^{(3)}$ from the structure of L . In addition, there are no higher order terms than these already coming from the structure of L itself. Hence, we may conclude that the factorization exactly truncates at its second order terms if we retain $\underline{\sigma}^{(3)} \otimes \underline{L}^{(3)}$ as a global second degree Lie operator. Indeed, if we write

$$\begin{aligned} Q\underline{x} &= \exp[\underline{x}^T \underline{f}^{(1)} \cdot \underline{\nabla}] \exp[\underline{\sigma}^{(3)} \otimes \underline{L}^{(3)}] \underline{x} \\ &= \exp[\underline{x}^T \underline{f}^{(1)} \cdot \underline{\nabla}] \frac{r}{[1 - 2\sigma_3(t)r^2]^{\frac{1}{2}}} \begin{bmatrix} \cos \theta \\ \sin \theta \end{bmatrix}, \end{aligned} \quad (\text{IV.18})$$

then it follows that

$$Q\underline{x} = \frac{e^{\lambda t}}{\left[1 + (e^{2\lambda t} - 1) \frac{x_1^2 + x_2^2}{\lambda} \right]^{\frac{1}{2}}} \begin{bmatrix} \cos t & -\sin t \\ \sin t & \cos t \end{bmatrix} \begin{bmatrix} x_1 \\ x_2 \end{bmatrix} \quad (\text{IV.19})$$

and the exact result is obtained. In this result we have first used polar coordinates

$$\begin{aligned} r &= [x_1^2 + x_2^2]^{\frac{1}{2}} \quad \cos \theta = x_1 [x_1^2 + x_2^2]^{-\frac{1}{2}}; \\ \underline{\sigma}^{(3)} \otimes \underline{L}^{(3)} &= \sigma_3(t) r^3 \frac{\partial}{\partial r} \end{aligned} \quad (\text{IV.20})$$

and then returned to the cartesian representation in Eq. (IV.19).

The result in Eq. (IV.19) is just a confirmation of the operator algebra introduced earlier in the paper. We may still go a step further and factorize the evolution operator involving $\sigma^{(3)} \circ L^{(3)}$ to obtain

$$Q^{(2)} = \exp[\sigma_3(t) x_1^3 \frac{\partial}{\partial x_1}] \exp[\sigma_3(t) x_1^2 x_2 \frac{\partial}{\partial x_2}]$$

$$\exp[\sigma_3(t) x_2^2 x_1 \frac{\partial}{\partial x_1}] \exp[\sigma_3(t) x_2^3 \frac{\partial}{\partial x_2}]$$

(IV.21)

This different factorization creates an error which is of the order of magnitude of fifth degree terms. In this case, an infinite product appears which converges about the origin.

v) space extension

Consider the system defined by the function

$$f(x) = \sqrt{1-x^2} \quad (IV.22)$$

This function has two zeros located at the points $x=+1$ and $x=-1$, however it does not fulfill the requirements for our method. In particular, it cannot be expanded in a Taylor series around these points. Nevertheless, the problem may still be approached by extending the space to two dimensions through the introduction of a new variable in addition to x as follows

$$y = \sqrt{1-x^2} \quad (IV.23)$$

We can now define a new system with the descriptive functions

$$f_1(x,y) = y$$

$$f_2(x,y) = -x \quad (IV.24)$$

This new system satisfies all of the necessary conditions for factorization. Therefore, in cases such as these, the technique of space extension may make it possible to factorize Lie transformations which otherwise might not admit to direct treatment.

V. CONCLUDING REMARKS

The basic thrust of this paper is the development of a new sequence of approximants appropriate for time evolution operators with Lie generator arguments. Although we have not given convergence theorems for the ξ -approximants sequences, the results in Section IV are encouraging. Rapid and highly accurate convergence seems to be obtained at least in a sufficiently closed vicinity to the origin. The next step in this work, examined in a companion paper, is the investigation of the ξ -approximant singularities and some convergence theorems.

Actual implementation of the factorization scheme, especially for multidimensional cases can involve a considerable amount of algebra. The use of symbolic programming on the computer would likely be a necessity in these cases, and this issue also needs further investigation for its practical implementation. A number of applications of the factorization may be envisioned as suggested in the introduction. Evolution operators of the type studied in this paper occur in a wide variety of problems, but perhaps the most obvious and simple application would be to the solution of ordinary differential equations. The possible attraction here follows from the fact that the approximants provide a global solution in time rather than the usual sequential time stepping procedures. A number of numerical issues need to be addressed for this case as well as other applications before the optimal realm of utility of the scheme may be established.

Acknowledgment

The authors would like to thank Professor Carl Wulfman for helpful comments. We also acknowledge support from the Office of Naval Research and the Air Force Office of Scientific Research.

Figure Captions

- Figure 1** Plot of the exact deviation function $\xi(x,t)$ and its first five approximants $\xi_n(x,t)$, $n=1,\dots,5$ for the characteristic function in Eq.(IV.1) where $x=0.1$. In figure a, the last three approximants are indistinguishable from the exact result. Figure b shows the deviation function for the approximant $n=5$. The same line masks in figure a will be used in the remaining ξ -approximant plots.
- Figure 2.** The same as figure 1, except $x=5.0$. These results are qualitatively similar to those of figure 1 except now the convergence rate is slower and there is a peak in the error function.
- Figure 3.** The same as figure 1, except now $x = -1.0$. Apparent oscillatory nonmonotonic behavior is exhibited with respect to the true deviation function in figure a.
- Figure 4.** Figure a exhibits the exact deviation function $\xi(x,t)$ and the first five approximants $\xi_n(x,t)$, $n=1,\dots,5$ corresponding to the fundamental function in Eq. (IV.3) at $x = 0.1$. Figure b shows the error function for $n=5$ approximant. Apparent divergence behavior is observed at long time; however, during a finite interval around the origin there is temporary convergence. Here, only the fifth approximant goes to infinity. However, the first four approximants also have branch points

close to zero but they do not make the denominator in the corresponding transformation from the previous approximant zero when $t < 10$. Some of the branch points are not even on the positive real axis.

Figure 5. The exact deviation function $\xi(x,t)$ and its first five approximants $\xi_n(x,t)$, $n=1,\dots,5$ for the characteristic function in Eq. (IV.5) at $x=1.0$. The first and second approximants coincide as well as the third and fourth approximants. There is apparent convergence behavior in Figure a, however a peak in the error function in Figure b may signal a loss of global convergence.

Figure 6. The same as Figure 5, except that now $x=5.0$.

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Figure 1a

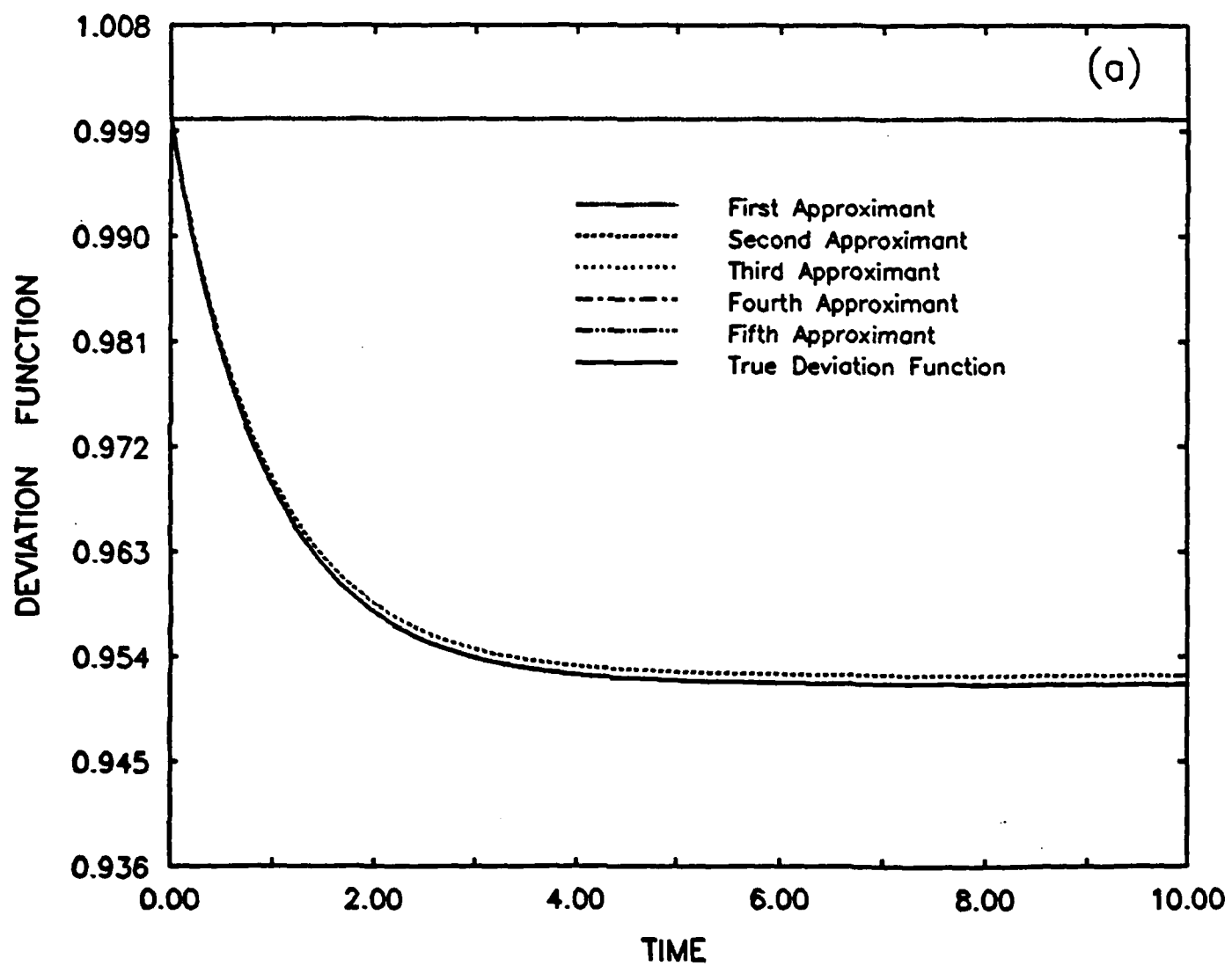


Figure 1b

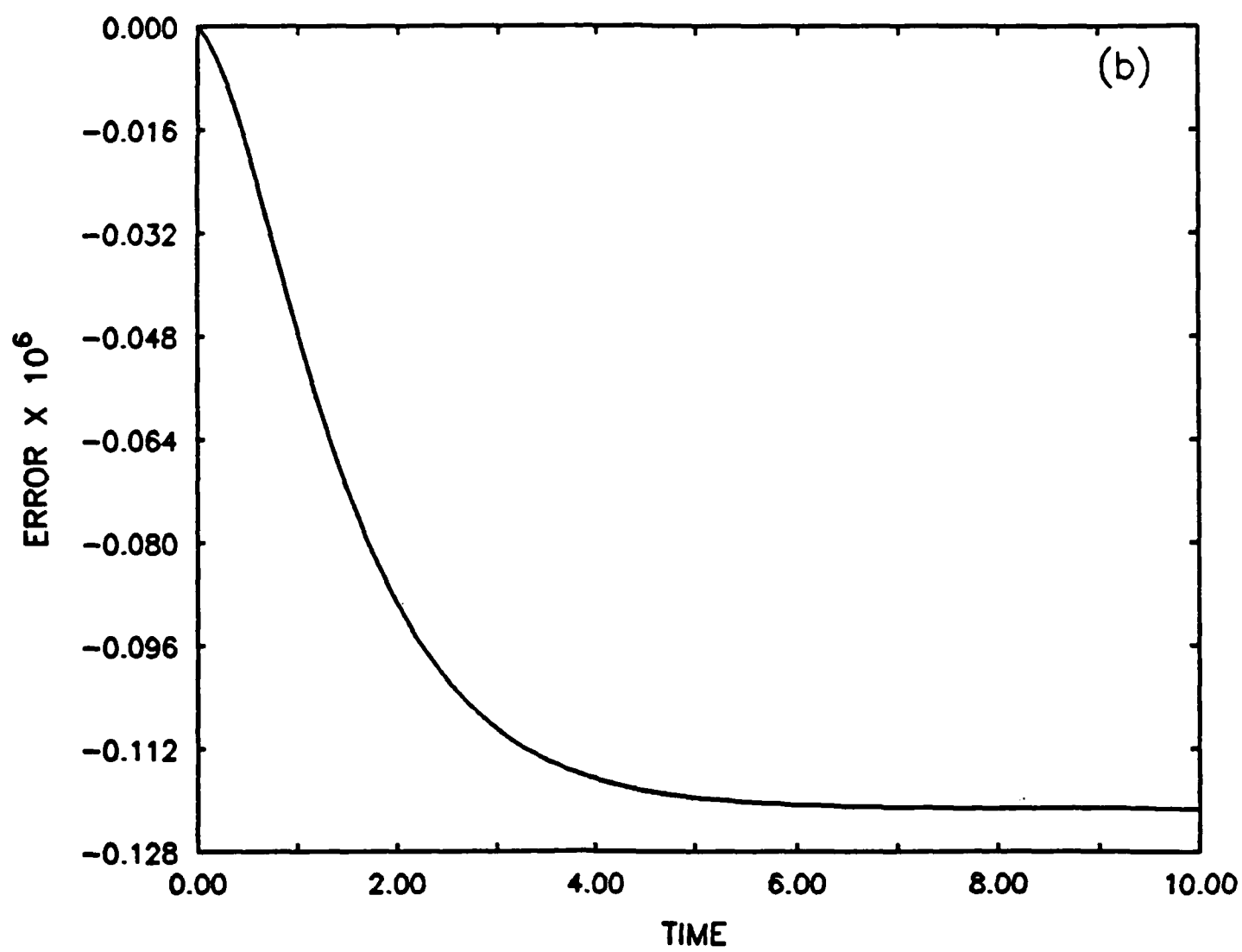


Figure 2a

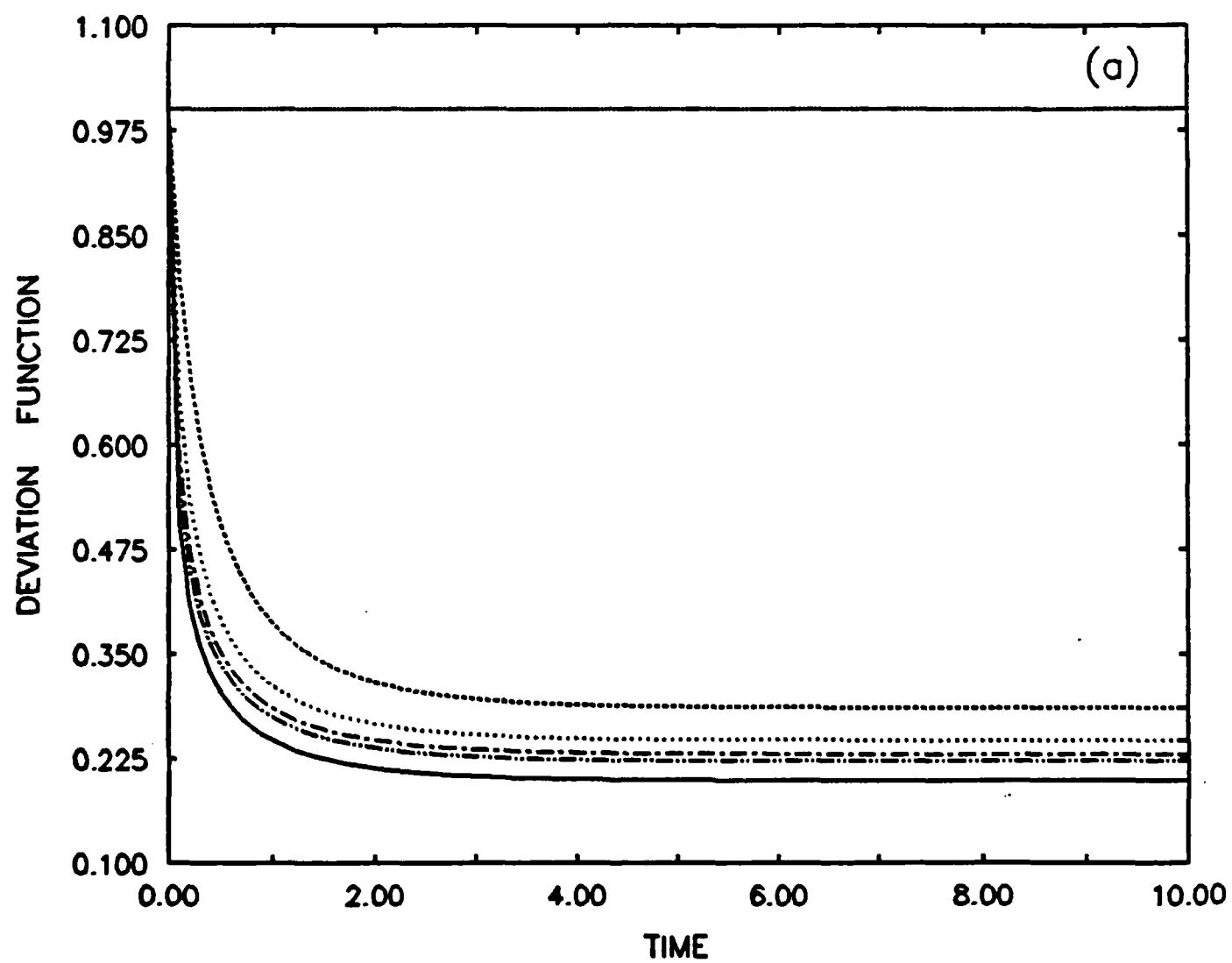


Figure 2b

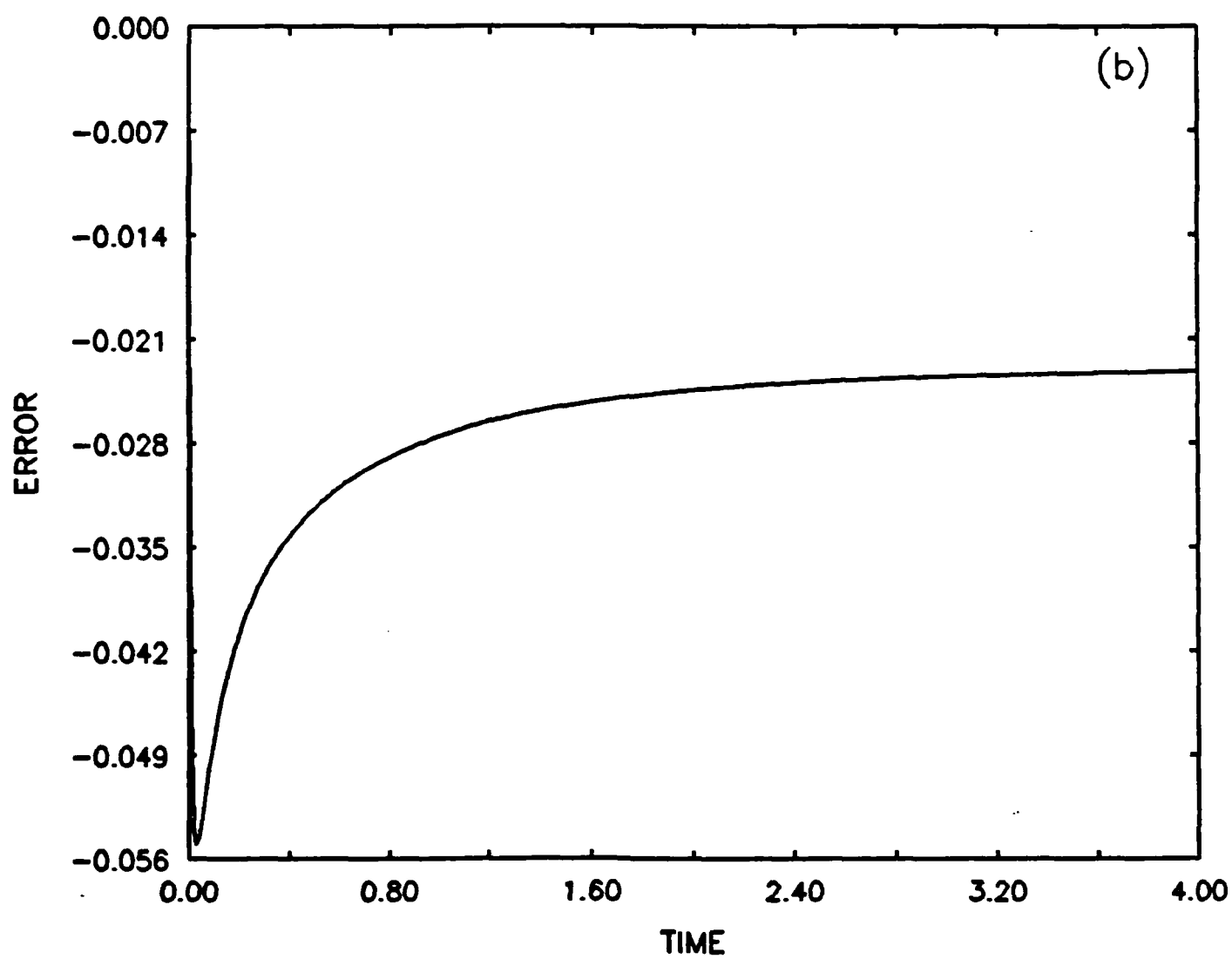


Figure 3a

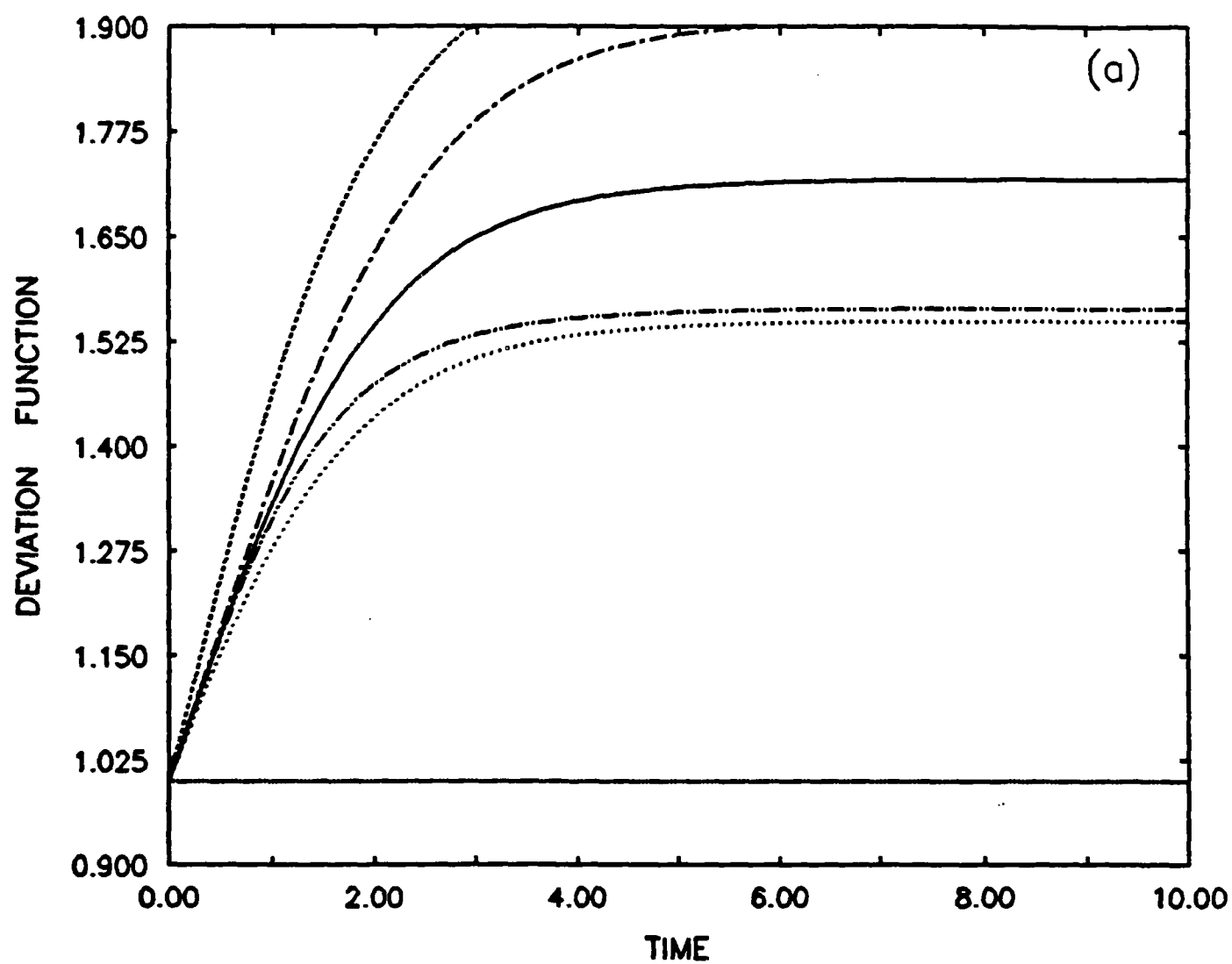


Figure 3b

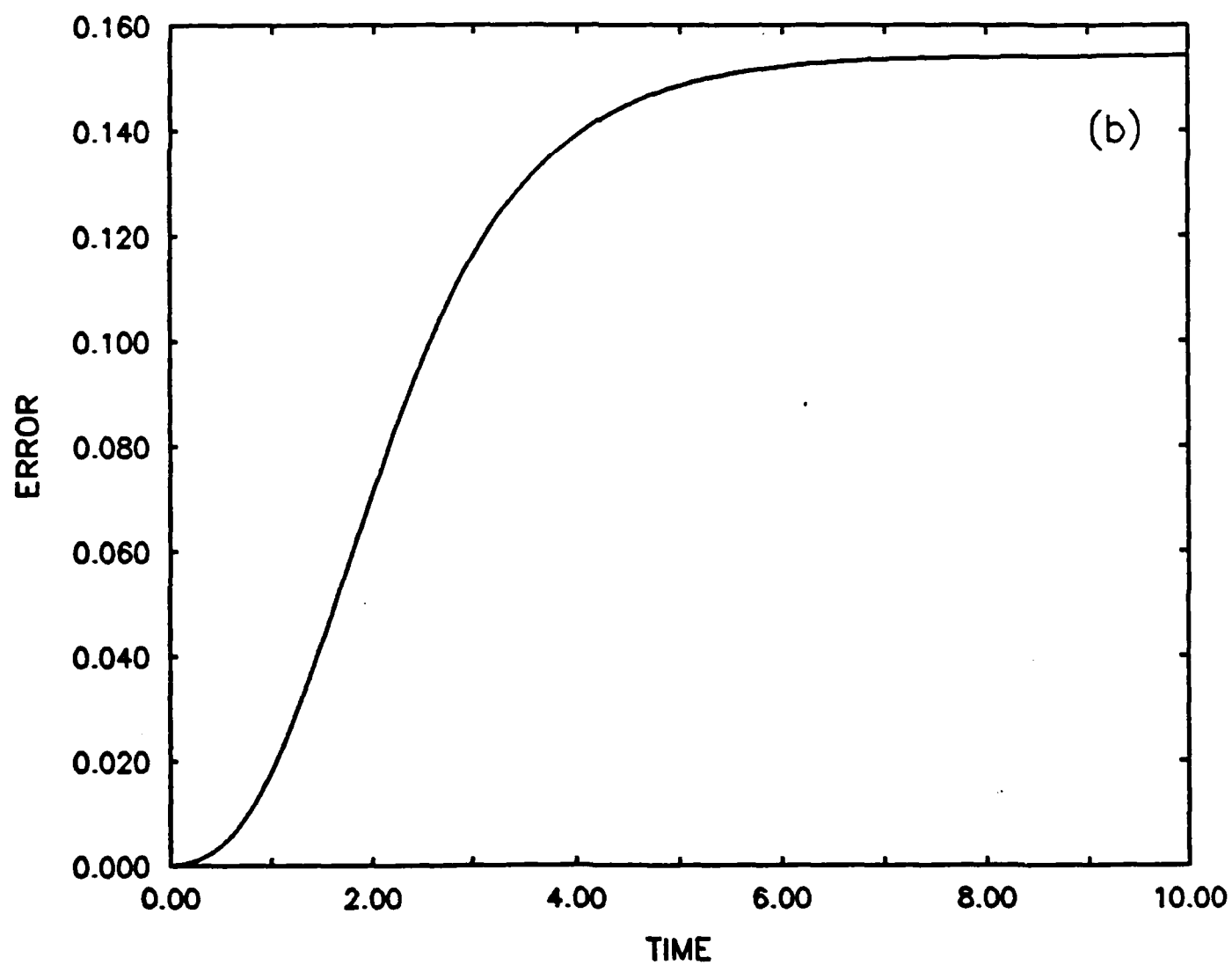


Figure 4a

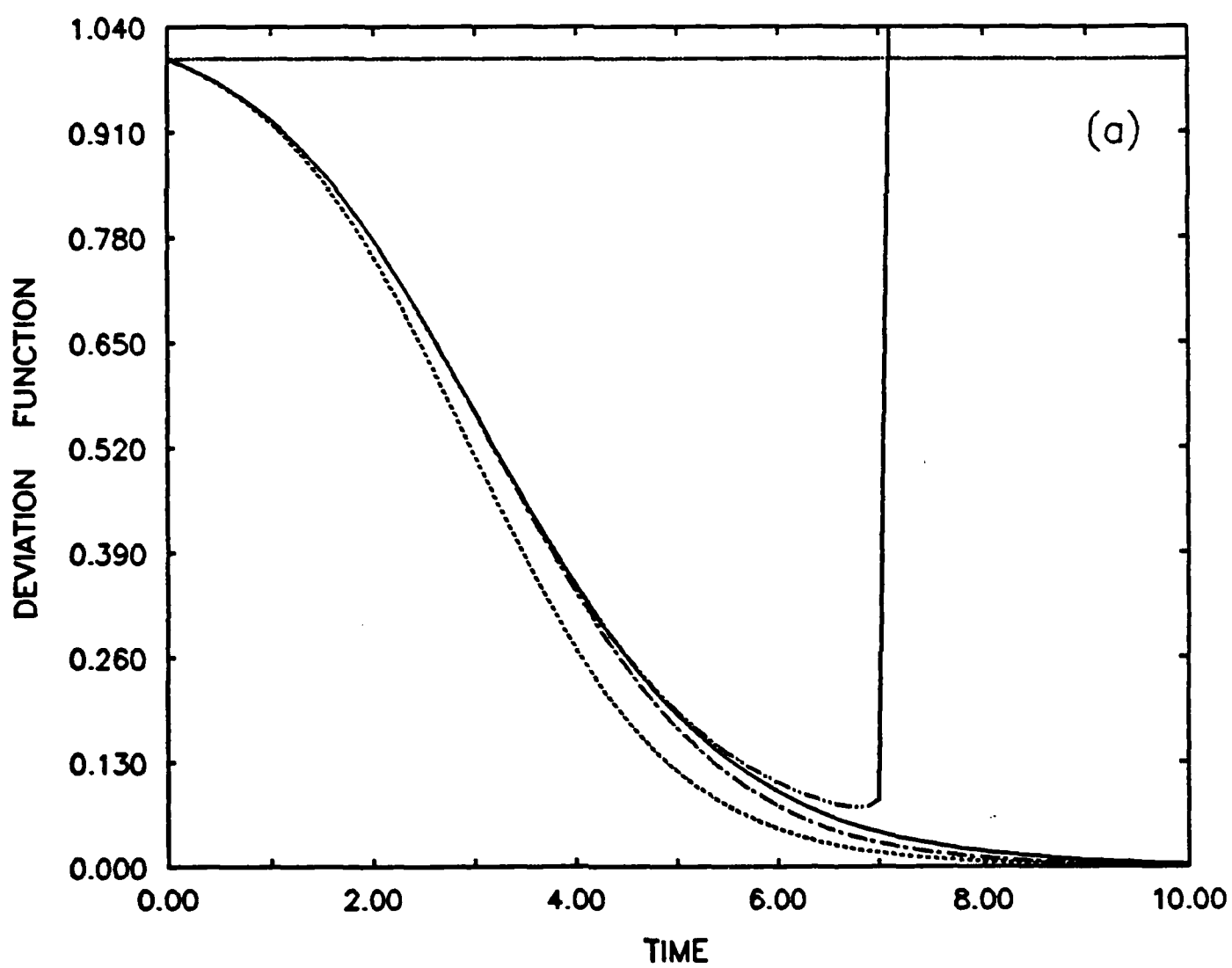


Figure 4b

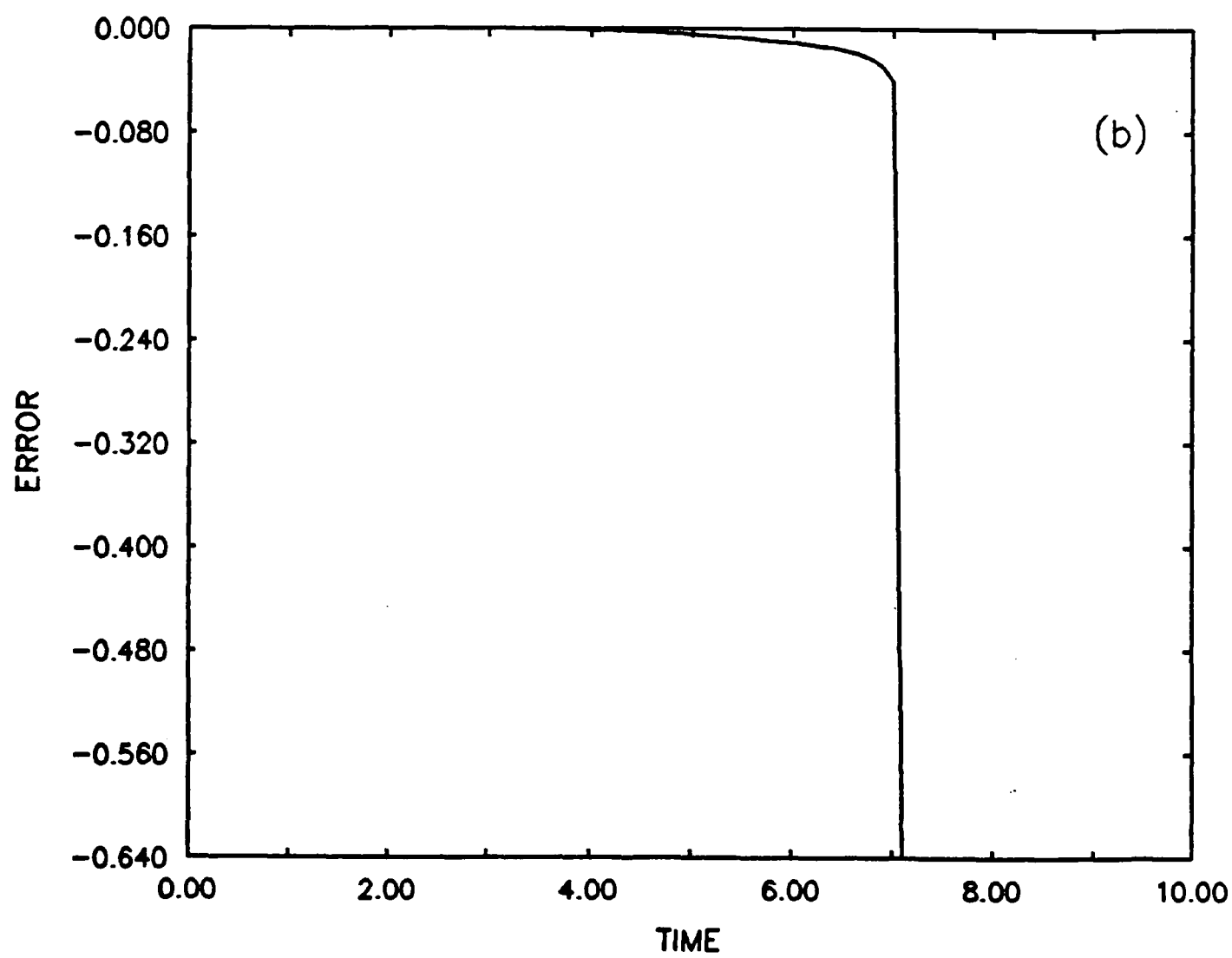


Figure 5a

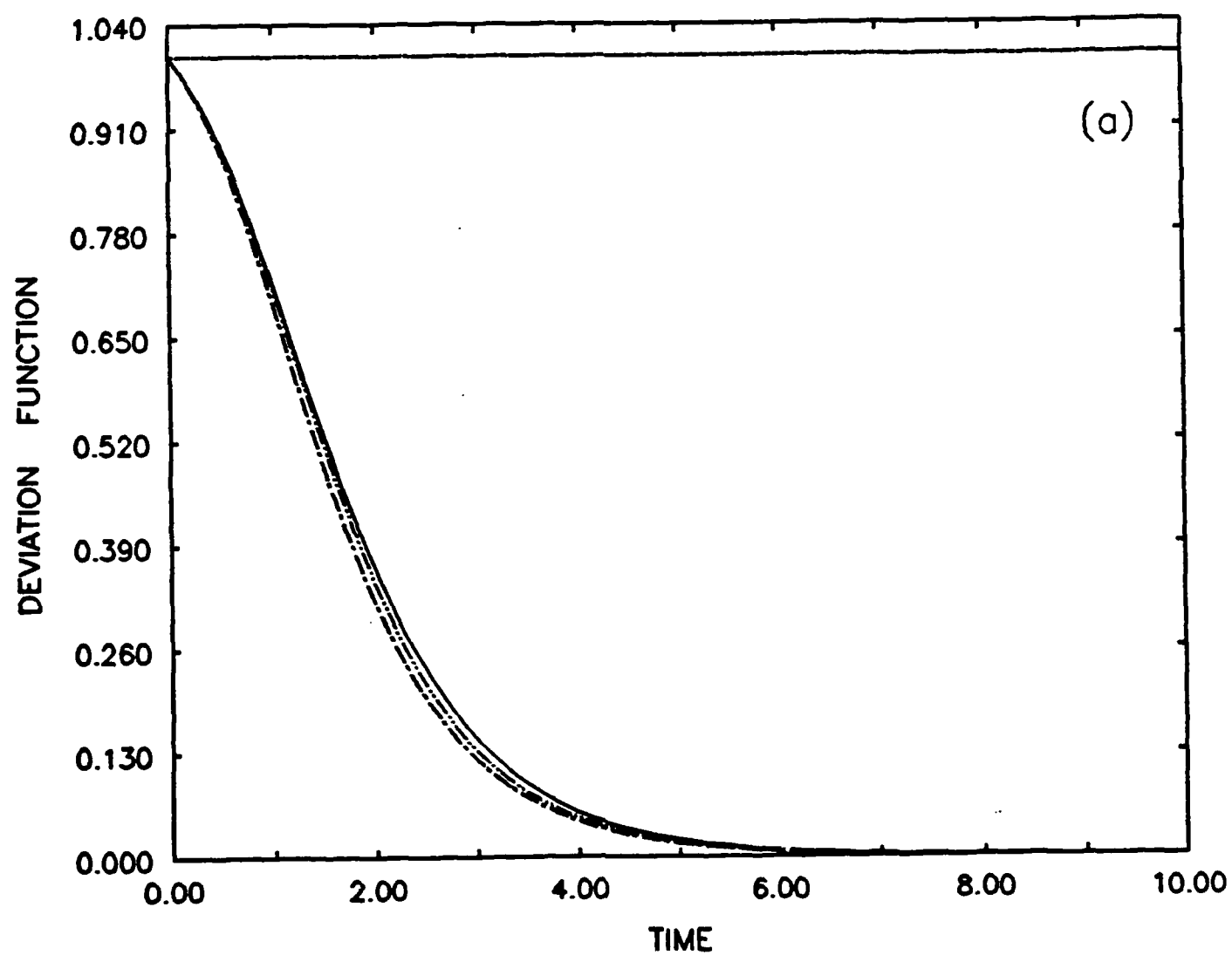


Figure 5b

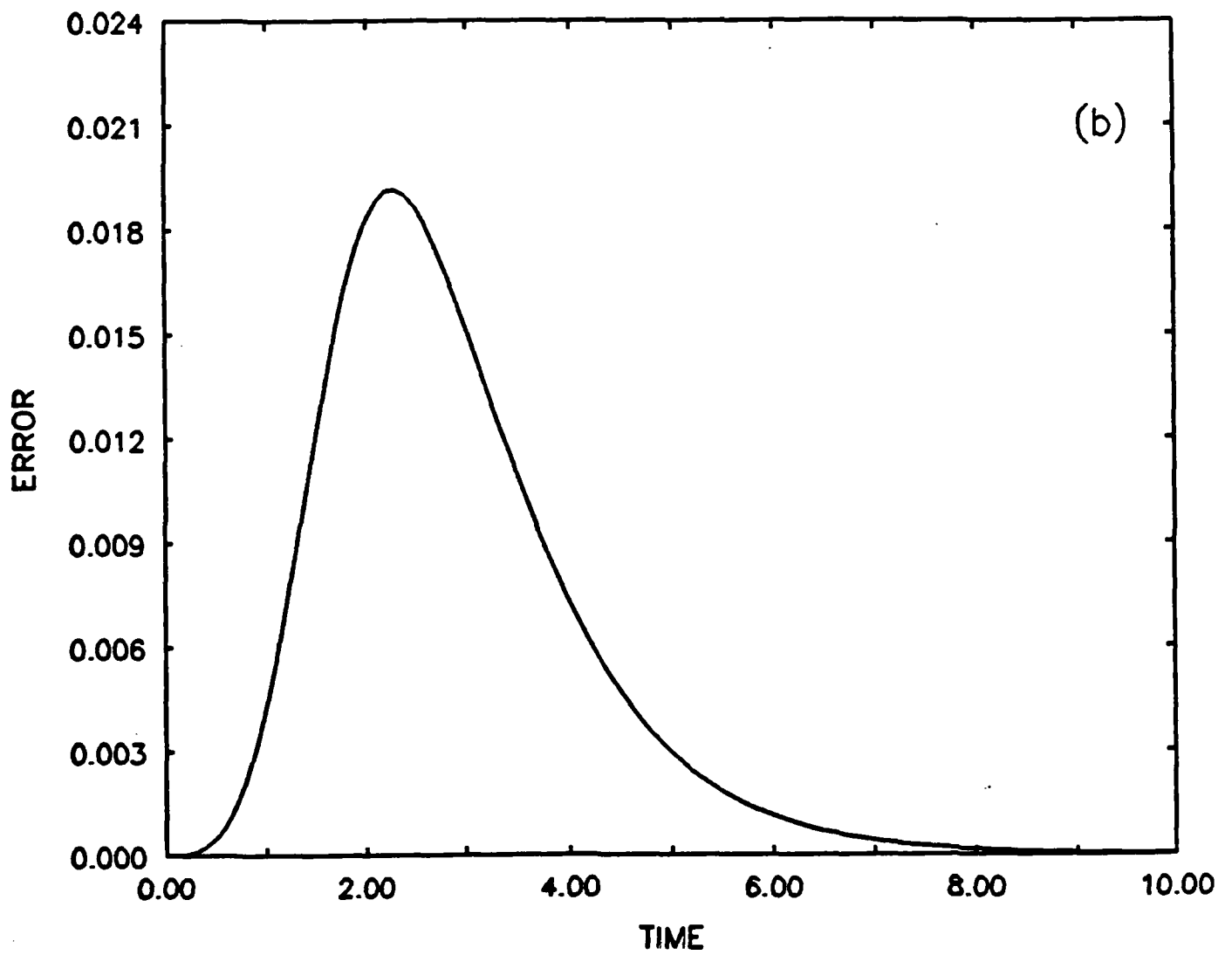


Figure 6a

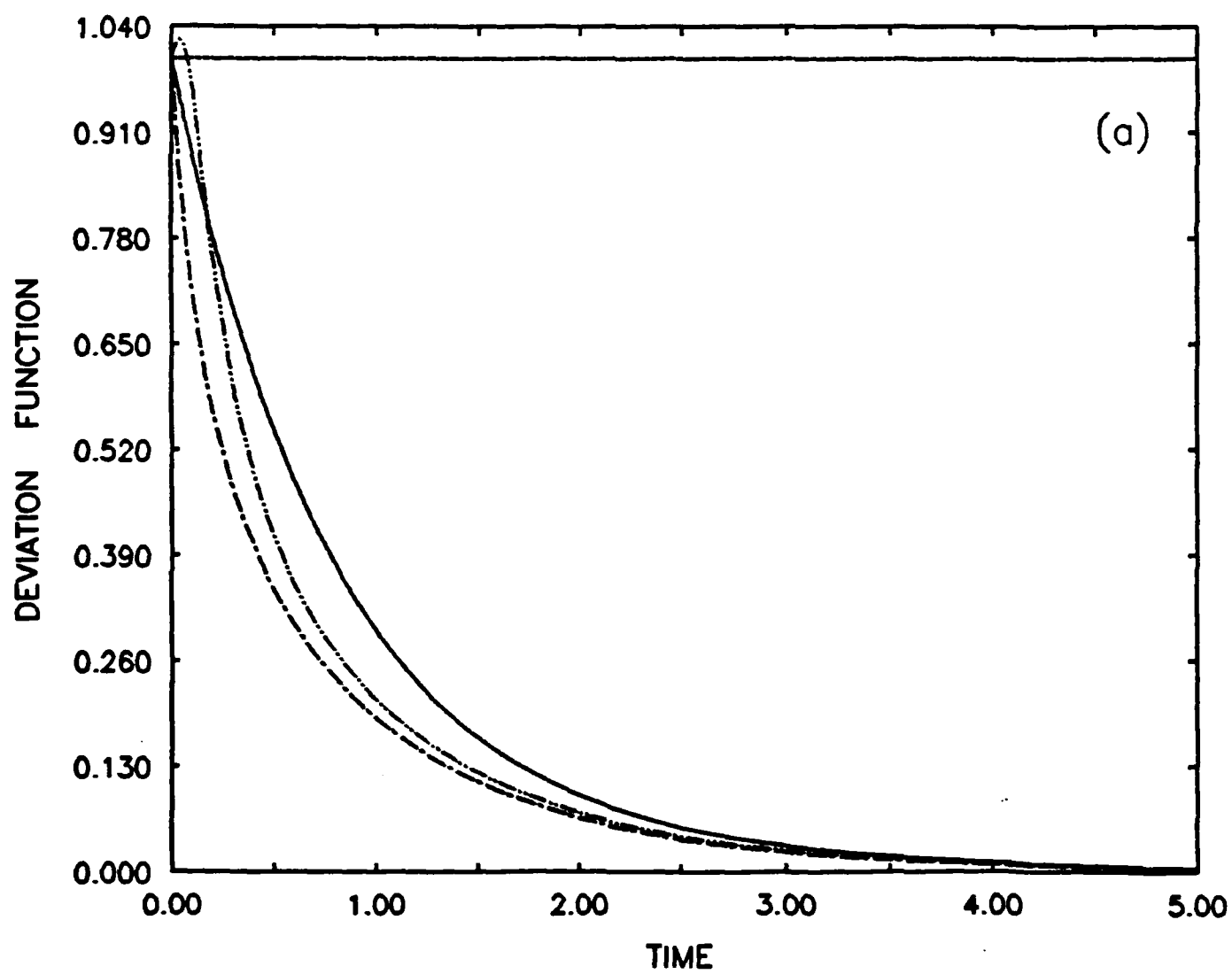
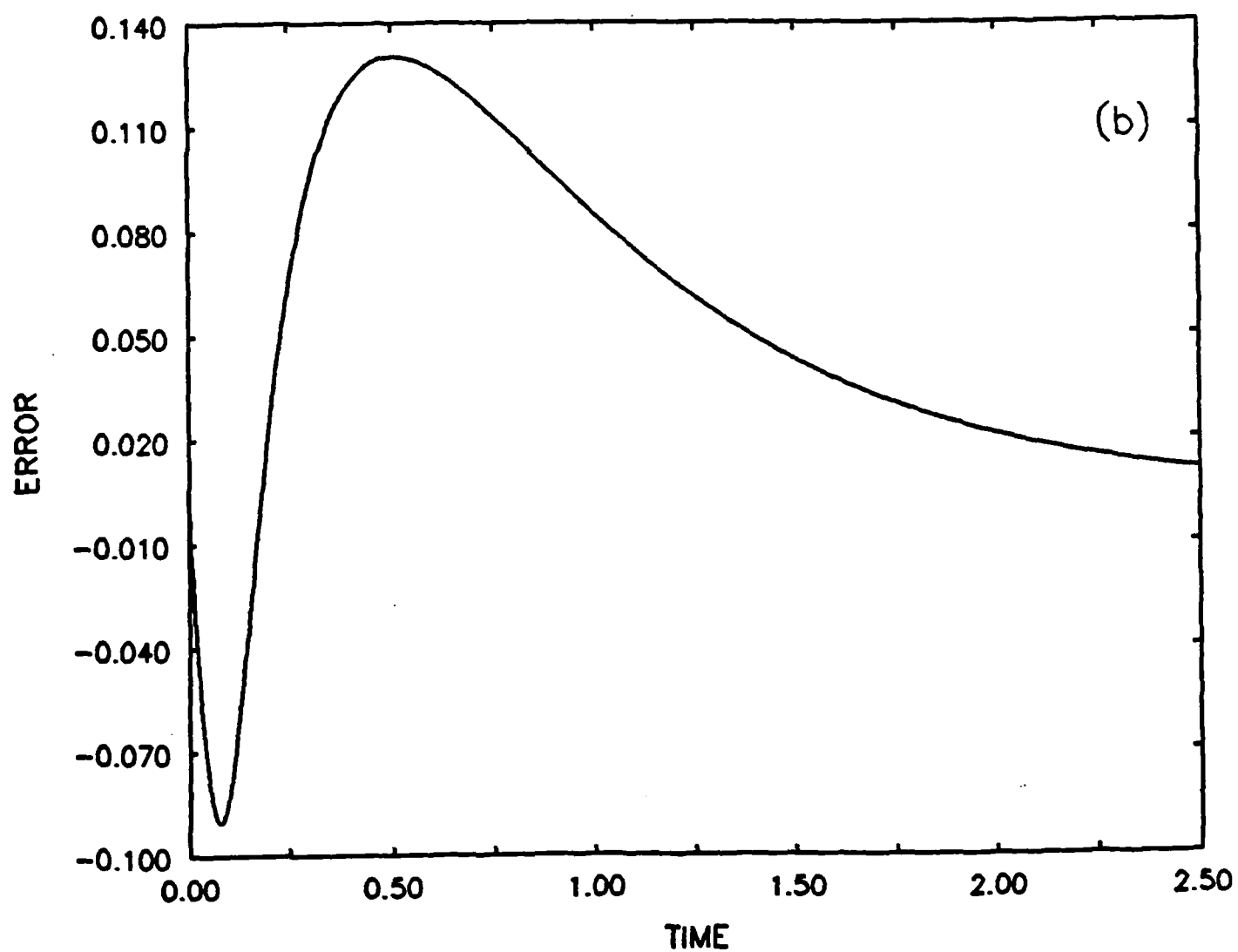


Figure 6b



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COMPLICATIONS OF ONE-STEP KINETICS FOR
MOIST CO OXIDATION

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(17) Kinetics

(18) Modeling and Scaling

(24) Chemical Mechanisms

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COMPLICATIONS OF ONE-STEP KINETICS FOR MOIST CO OXIDATION

Abstract

The one-step reaction mechanism, $\text{CO} + \frac{1}{2} \text{O}_2 \rightarrow \text{CO}_2$ with

$$d[\text{CO}]/dt = -k_{\text{ov}}[\text{CO}]^a[\text{H}_2\text{O}]^b[\text{O}_2]^c$$

which is frequently used in combustion problems when simplified chemistry is necessary, is numerically studied in order to (i) define its limitations (and therefore usage) and (ii) understand the chemical and physical reasons for these limitations. The analysis is carried out with the aid of a validated comprehensive, elementary reaction mechanism for moist CO oxidation and by specialized sensitivity coefficients which correlate the parameters of the global model to the parameters of the elementary model. The results confirm many of the previous, empirically derived, literature models and show the overall rate constant, as a function of temperature, to exhibit non-Arrhenius kinetics and to be dependent on pressure and mixture equivalence ratio. More importantly, models derived from temporally reacting systems are shown to be improper for use in modeling systems reacting with transport phenomena. The specialized sensitivity coefficients are used to explain these complex behaviors in the overall model. For the temporal system, these coefficients show that the global model must be able to account for dissociation and equilibration at high temperatures, for explosion phenomena in the intermediate temperatures, and for reaction of carbon monoxide with both the hydroxyl radical and hydroperoxy radical at low temperatures. Lastly, methods for modifying the existing model or for developing a new model are suggested.

INTRODUCTION

The commonly accepted one-step reaction mechanism for moist carbon monoxide oxidation consists of the overall chemical equation, $\text{CO} + \frac{1}{2} \text{O}_2 \rightarrow \text{CO}_2$, with the reaction rate for CO disappearance defined as $-d[\text{CO}]/dt = k_{\text{ov}}[\text{CO}]^a[\text{H}_2\text{O}]^b[\text{O}_2]^c$. Typically, the overall specific rate constant is expressed in Arrhenius form as $k_{\text{ov}} = A_{\text{ov}} \exp(-E_{\text{ov}}/RT)$.

Since first postulated in 1956¹, the global parameters, A_{ov} , E_{ov} , a , b , and c , of this model have been empirically derived by numerous research groups from various experiments. Most recently (1985), Lyon et al.² have evaluated these parameters from flow reactor data for dilute mixtures of O_2 and H_2O with trace quantities of CO reacting in He around 1100 K and 1.2 atm. Their results and the selected results of others for different environmental conditions are presented in Table I. Quite evident from the table is a wide variation in parameter values. For example, compare Lyon's results with Dryer's results obtained for similar experimental conditions, but with different levels of initial CO concentration. Or compare all of the values (particularly the overall activation energies) as a function of increasing experimental temperature. It is apparent, a unique parameter set does not exist, especially for the range of environmental parameters encountered in most combustion problems. Regardless of whether these variations are attributed to experimental problems or to changes in the elemental chemical mechanism, this model continues to be used (mainly for lack of a better model) in many applied combustion problems.³

The objectives of the present paper are to explore the complex character of this one-step mechanism. In particular, (i) What are the limitations of the model and under what circumstances can it be used?, (ii) Why does the model fail (e.g., is the failure a result of changes in the chemical mechanism structure, or of couplings between chemistry and transport phenomena)? and

(iii), How can the model be corrected (i.e., what new methods exist to modify and build future models)? The paper is organized in the order of the above three topics, and is summarized with concluding remarks.

Finally, from a more general perspective this paper proposes and demonstrates new mathematical techniques for the analysis and construction of global models. The term global, as used here, is synonymous with terms such as "reduced" and "lumped", which are expressions commonly used outside the field of combustion.⁴ Hence, the applicability of the mathematical theory discussed here covers considerably more subject areas than the combustion kinetics field for which it is demonstrated.

LIMITATIONS OF THE GLOBAL MODEL

Generally, global combustion models are constructed using experimental data from a wide range of sources.⁵ Until recently, this process, shown pictorially in Fig. 1 as path "a", has been limited to the left hand side of the dashed line. Typically, the methodology of "a" would consist of least squares fitting an a priori known function to measured experimental data. Advances in the development of elementary reaction mechanisms, along with increasingly more efficient computer codes, have made it now possible to generate global parameter models from the data bases of elementary systems.⁶ In Fig. 1, this process is represented by the clockwise perimeter line, paths "b & c". At this point, it is important to recognize that path "c" can be interpreted as an analogue to path "a", or as will be discussed later, can involve systematic methods for developing global models (i.e., methods for determination of both the governing equations and parameters).

The development of elementary models (path "b") is a subject outside the scope of this work.⁷ For the present discussion, it is sufficient to only assume the existence of such a model. Currently, fuel molecules for which the detailed combustion chemistry can be described with confidence have at most

three carbon atoms;⁸ butane through octane combustion models are topics of exploratory research.^{9a,b} Surely, continued progress in this area can be anticipated, but it should also be emphasized here that complete comprehensive reaction mechanisms are not a necessary criteria for the success of the present work.

Most combustion problems may be described in generalized form by the vector set of differential equations,

$$\underline{L}(\underline{Q}^d, \underline{\alpha}) = 0, \quad (1a)$$

where $\underline{Q}^d(x, t, \underline{\alpha})$ is the vector of dependent variables (species concentrations, temperature, etc.) desired by solution of Eq. (1a) and L_i ($i=1, \dots, N_\alpha$) is an appropriate differential operator for the i -th dependent variable. Here, the superscript "d" refers to the elementary (or detailed) model, and the vector $\underline{\alpha}$ includes all the input parameters of the model. The independent variables of space and time are denoted as x and t , respectively.* Depending upon the particular problem, numerous computational codes are currently available for the solution of Eq. (1), e.g., for temporally reacting systems,^{10,11} for steady premixed flames,¹² for unsteady premixed flames,¹¹ for diffusion flames,¹³ etc.

In the present work, the recent elementary reaction mechanism of Yetter et al.^{14a,b} for describing carbon monoxide / hydrogen / oxygen kinetics is employed. This elementary reaction mechanism, consisting of 11 chemical

* A parallel system of equations exist for the global model,

$$\underline{L}(\underline{Q}^g, \underline{\beta}) = 0, \quad (1b)$$

where the superscript "g" denotes global and the vector $\underline{\beta}$ includes all the input parameters of this model. By definition, $N_d > N_g$ and $N_\alpha > N_\beta$.

species and 27 reversible elementary reactions, has been validated over a combined temperature range of 800 - 2800 K, fuel - air equivalence ratios between 0.001 and 6, and pressures between 0.3 and 3 atmospheres. Thus, the overall rate constant can be determined for any set of environmental parameters using numerically generated data from the detailed calculations. For example, Fig. 2a shows the overall rate constant as a function of inverse temperature. Here the values of a , b , and c were taken from Dryer and Glassman as 1, 0.5, and 0.25, respectively. These parameters have been obtained experimentally by several other research groups as well (see Table I), and in addition, Fristrom and Westenberg⁵ and Dryer¹⁵ note that the same parameters are obtained if a number of reactions involving the radical species H, O, and OH are assumed microscopically balanced and the conversion of CO to CO₂ occurs only by way of $\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H}$.^{*} For example, if the two reactions, $\text{O} + \text{H}_2\text{O} \rightleftharpoons 2\text{OH}$ and $\text{O}_2 + \text{M} \rightleftharpoons 2\text{O} + \text{M}$, are assumed in partial equilibrium, the above values for a , b , and c are obtained when the associated equilibrium equations are solved for the hydroxyl radical concentration and substituted in the rate equation for the reaction between CO and OH. One should be very cautious as to the universality of these parameters since Dryer's experiments were conducted at extremely fuel lean conditions. Furthermore, many of the elementary reactions involving H, O, and OH radicals have been shown previously to be balanced only for fuel lean conditions.^{14b}

The results presented in Fig. 2a were obtained from numerous isothermal

*The fact that this reaction is generally the slow, rate-determining (and often dominating) step of the elementary reaction mechanism has been used by many to justify the applicability of the current one-step reaction mechanism.

calculations using a dilute mixture of CO, O₂, and H₂O in N₂ in which only the reaction temperature was varied. The value plotted at a given reaction temperature represents a mean value ($\int k_{ov}(t) dt / \int dt$) over a period during which approximately 90% of the deficient species was consumed (CO for $\phi \leq 1$ and O₂ for $\phi > 1$). This interval excluded both induction and equilibrium chemistry. Typically, the variation in k_{ov} over this interval was less than $\pm 50\%$ of the average value. Obviously, k_{ov} does not exhibit an Arrhenius dependence over the complete temperature range of 770 to 2500 K. More importantly, the inferred results of E_{ov} over limited temperature ranges agree extremely well with the empirical values of E_{ov} obtained from various experiments.¹⁴ The predicted values of k_{ov} are also in good agreement with the appropriate empirical values. For example, at 1150 K Dryer and Glassman find $k_{ov}^{emp} = 9.7 \times 10^6 \text{ (cm}^3 \text{ mol}^{-1})^{3/4} \text{ s}^{-1}$ and the elementary model predicts $k_{ov}^d = 8.6 \times 10^6 \text{ (cm}^3 \text{ mol}^{-1})^{3/4} \text{ s}^{-1}$ and at 1400 K Hottel et al. find $k_{ov}^{emp} = 3.9 \times 10^8 \text{ (cm}^3 \text{ mol}^{-1})^{3/4} \text{ s}^{-1}$ and the model predicts $k_{ov}^d = 2.9 \times 10^8 \text{ (cm}^3 \text{ mol}^{-1})^{3/4} \text{ s}^{-1}$.*

Similar plots of k_{ov} for variations in pressure, equivalence ratio, and water vapor concentration are shown in Figs. 2b, 2c, and 2d, respectively. For variations in these physical parameters, the global model is expected to exhibit a constant overall rate constant. The figures themselves may be examined to study the range over which the global mechanism applies.

The results of Fig. 2 clearly demonstrate that if the global parameters of the one-step mechanism are evaluated at a specific operating point (i.e., specific temperature (T), pressure (P), equivalence ratio (ϕ), mixture

*The model predictions reported here are based on mixtures studied by the respective authors.

composition (c_i)), significant errors can result in predictions at operating points other than where the model was originally calibrated. The most significant error would occur in a system with a large change in temperature. Moreover, all the overall rate constants presented in Fig. 2 have been obtained for temporally reacting systems. Systems such as these have often been used to evaluate the global parameters; the intent of many of these studies has been to develop global models which could be later used to predict the same chemistry, but in more complex environments (e.g., premixed and diffusion flames, internal combustion engines, gas turbines, etc.). The natural question at this point is thus, what is the behavior of k_{ov} in a more complex environment?

Figure 3 shows the results of the overall rate constant obtained from two reacting systems, one of which is a laminar premixed flame and the other, an adiabatic flow reactor. For both cases, the initial mixture composition was the same. In this figure, k_{ov} is not averaged, but is plotted as a function of increasing reaction temperature. The values plotted correspond to the interval (i.e., positions in the flame or reactor) from 5 to 95% consumption of O_2 .^{*} Discrepancies exist at both low and high temperatures, which dramatically show the influence of diffusion on the chemistry. As a consequence, global models derived in one environment may not be applicable to another. To emphasize this point further, Bilger¹⁶ has shown that, in laminar diffusion flames, k_{ov} exhibits a negative temperature dependence!

*Note that the complex behavior of k_{ov} vs. inverse temperature for the exothermic adiabatic flow reactor is similar to the dilute isothermal reacting system of Fig. 2a.

The behavior of k_{ov} for numerous other systems/environmental conditions can be readily obtained from detailed calculations. The results presented thus far have convincingly shown that the current model is limited and should be applied, using the information of Figs. 2 and 3, with considerable caution. Further computations support these findings, but do not explain their occurrence. In the next section, specialized correlation coefficients are derived and analyzed to understand these anomalies.

MODEL ANALYSIS

Returning to Fig. 1, sensitivity analysis theory has played a central role (paths "d & e") in the development and analysis of detailed elementary reaction mechanisms.¹⁷ The same theories are applicable to global model development (via path "f"), yet sensitivity analysis has had only limited usage in this area.

Furthermore, the combined connection, path "d-f", has never been explored. The latter connection enables the possibility of relating the parameters of global models to the parameters of elementary models. Such information is useful for a better understanding of existing global schemes and to address the necessary questions for improving or developing new models, e.g., what lumping parameters should be employed, and what should be the functional character of the lumping equations?

The role of elementary sensitivity analysis enters as a means for assessing the importance or contribution of the various system parameters β with respect to objectives of interest. The coefficients,

$$S_{ij} = \partial \phi_i(x, t, \beta) / \partial \beta_j,$$

provide a direct measure of how the j -th parameter controls the behavior of the i -th dependent variable at point x and time t .

The equation that the first order elementary sensitivity coefficients satisfy is

$$\sum_{n=1}^N (\partial L_i / \partial O_n^g) (\partial O_n^g / \partial \beta_j) + (\partial L_i / \partial \beta_j) = 0. \quad (2)$$

The solutions may be conveniently expressed in terms of the system Green's function defined to satisfy the following equation,¹⁸

$$\sum_{n=1}^N (\partial L_i / \partial O_n^g) G_{nn'} = \delta_{in'}(x-x') \delta(t-t'), \quad (3)$$

whereby the solution to Eq. (2) may now be expressed in terms of the Green's function,¹⁸

$$S_{ij}(x,t) = \sum_{n=1}^N \int_{x_1}^{x_2} dx' \int_{t_1}^{t_2} dt' G_{in'}(x,t;x',t') \partial L_{n'}(x',t') / \partial \beta_j. \quad (4)$$

A similar equation is derivable for the second order elementary sensitivity coefficients, $\partial^2 O_i^g / \partial \beta_j \partial \beta_k$, which is again solvable by the Green's function method.¹⁸ Although elementary sensitivity coefficients are not the subject of the present section, they are required for evaluation of the correlation coefficients, and by themselves, are a valuable tool for model analysis. For example, an analysis of Dryer's model shows that the most important parameter on the CO concentration profile is the overall activation energy, E_{ov} , whereas for Lyon's model, the most important parameter is the CO concentration exponent, a .

At this point, it should be evident from the preceding discussion that any dependent variable occurring in both the global and elementary models can be represented by the two equivalent forms,

$$O_i^g(\underline{\beta}) \equiv O_i^d(\underline{\alpha}).$$

A functional relationship between the vectors of global and elementary parameters is consequently implied,

$$\underline{\beta} = \underline{\beta}(\underline{\alpha}). \quad (5)$$

The goal now is to analyze the above equation and to determine as much as possible about the relationship between these two vectors. Note that the elementary parameters have to be chosen at some operating point $\underline{\alpha}^0$ in $\underline{\alpha}$ parameter space. (For the present analysis, it was assumed that $\underline{\alpha}^0$ was the optimum set of parameters from Ref. 14). The observable profiles and the

first order elementary sensitivity coefficients at the reference point in $\underline{\alpha}$ parameter space, $O_i^d(\underline{\alpha}^0)$ and $(\partial O_i^d / \partial \alpha_j)_{\underline{\alpha}^0}$, are readily evaluated, (by the parallel equations to Eqs. (2), (3) and (4)), which furthermore implies that the $\underline{\beta}$ vector and its gradient at the reference point, $\underline{\beta} = \underline{\beta}(\underline{\alpha}^0)$ and $(\partial \beta_i / \partial \alpha_j)_{\underline{\alpha}^0}$, may be determined.

The method for calculating these two quantities consists of utilizing Eq. (5) by defining a least squares (or alternatively, any other minimizing functional) in order to determine the $\underline{\beta}$ vector.

$$R_i = \sum_{\ell=1}^m \int_{t_1}^{t_2} dt \int_{x_1}^{x_2} dx [1 - (O_{i\ell}^g / O_{i\ell}^d)]^2 \quad (6)$$

The integrals in Eq. (6) are over the interval (or feature) of interest, $t_1 \leq t \leq t_2$ and $x_1 \leq x \leq x_2$. The flexibility in choosing this interval illustrates that the present analysis can be restricted to only those aspects of the problem of physical concern. The summation is over the number of experimental runs, "m" (in this case, modeling experiments), for which the global model is to be calibrated. In the present context, the index associating O_i^g and O_i^d with a specific run, ℓ , is omitted for notation convenience. Minimization of the residual in Eq. (6) can be achieved by differentiation with respect to the parameter β_j ,

$$0 = \sum_{\ell=1}^m \int_{t_1}^{t_2} dt \int_{x_1}^{x_2} dx [1 - (O_i^g / O_i^d)] (O_i^g / O_i^d) (\partial \ln O_i^g / \partial \ln \beta_j), \quad j=1, 2, \dots, N_\beta. \quad (7)$$

The solution of Eq. (7) implies the relation in (5), although again it must be emphasized that information on the elementary model is at the reference point $\underline{\alpha}^0$. Once again differentiating Eq. (7) with respect to the input parameters α_k , the following result is obtained,¹⁹

$$\sum_{n=1}^{N_\beta} Q_{in} (\partial \ln \beta_n / \partial \ln \alpha_k) = L_{ik}, \quad (8)$$

where

$$Q_{in} = \sum_{\ell=1}^m \int_{t_1}^{t_2} dt \int_{x_1}^{x_2} dx \quad (\gamma) [(1-2\gamma)(\partial \ln O_i^g / \partial \ln \beta_n)(\partial \ln O_i^g / \partial \ln \beta_j) + (1-\gamma)(\partial^2 \ln O_i^g / \partial \ln \beta_j \partial \ln \beta_n)],$$

$$L_{ik} = \sum_{\ell=1}^m \int_{t_1}^{t_2} dt \int_{x_1}^{x_2} dx (1-2\chi)(\chi) (\partial \ln O_i^g / \partial \ln \beta_j) (\partial \ln O_i^d / \partial \ln \alpha_k),$$
 and $\chi = (O_i^g / O_i^d)$. Eq. (8) is a set of linear algebraic equations determining the elements of the parameter-correlation, sensitivity coefficient matrix, $\partial \beta_n / \partial \alpha_k$. Note that the β vector should actually carry an additional index associating it with the i -th observable, and therefore the present analysis may be applied to any (or all) observables of the global mechanism.

When the fitting implied by Eq. (6) is sufficiently accurate, the second term in the integrand of Eq. (8) may be neglected and Eq. (8) can then be identified as having a least squares form for determining the parameter - correlation coefficients.

Returning to Figs. 2 and 3, the most dramatic deviation in the overall rate constant, away from its "expected" value, is the non-Arrhenius temperature dependence of Fig. 2a, and in the present section, the correlation coefficients described above are used to explain this observed, complex behavior. Three limited temperature ranges were studied: (i) $1600 \text{ K} \leq T \leq 2100 \text{ K}$, (ii) $900 \text{ K} \leq T \leq 1000 \text{ K}$, and (iii) $650 \text{ K} \leq T \leq 750 \text{ K}$. Since the largest variations in the empirical global parameters occur in the overall activation energy and the overall preexponential factor (see Table I), the present analysis concentrated on these two parameters; the parameters a , b , and c were taken from Dryer and were not determined from the least squares fit analysis. Thus, the analysis was simplified and the methodology stressed. Furthermore, the analysis was carried out with the same mixture (in mole fractions, $X(\text{CO}) = 0.01$, $X(\text{O}_2) = 0.20$, $X(\text{H}_2\text{O}) = 0.01$, $X(\text{N}_2) = 0.78$) and pressure (1 atm), varying only the initial temperature.

The global model, unlike the elementary model, does not have induction time kinetics. This complication is commonly remedied by introducing an induction time also in global form with another set of global parameters. In the present analysis, this period was defined by

$$\tau = B[\text{CO}][\text{H}_2\text{O}]^{0.5}[\text{O}_2]^{0.25}\exp(F/RT)$$

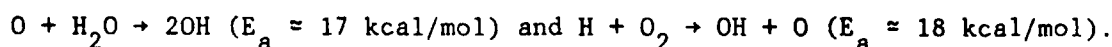
where the parameters B and F were determined by the least squares analysis, Eqs. (6) and (7). The concentration exponents were assumed to be the same as those for the oxidation process. Generally speaking, this assumption is not true (especially for the oxidation of hydrocarbons), and was applied here to illustrate the sensitivity analysis methodology. Again, in a more comprehensive analysis, the orders of the reaction could also have been determined through the least squares analysis.

The global parameters A_{ov} and E_{ov} were determined from the CO concentration profile using a time interval during which 90% of the CO was consumed. Specifically, t_1 and t_2 of Eq. (6) were defined as $[\text{CO}(t_1)]^d \equiv 0.95[\text{CO}(0)]$ and $[\text{CO}(t_2)]^d \equiv 0.05[\text{CO}(0)]$. Due to the absence of the induction time in the global model, a time shift was required to properly compare the two models. This time adjustment was made by shifting the results of the global model to match the CO concentrations of both models at $\frac{1}{2} [\text{CO}(0)]$. The parameters B and F were determined by defining τ as the time interval from $t=0$ to 5% consumption of the CO concentration.

In the high temperature regime, the least squares fit was conducted with data from six numerical runs with a combined total of over 200 points for comparison. The resulting least squares parameters for A_{ov} and E_{ov} were $1.06 \times 10^{11} (\text{cm}^3 \text{mol}^{-1})^{3/4} \text{s}^{-1}$ and 21 kcal/mol, respectively. Results from three of the numerical runs are shown in Fig. (4). The comparison between global and elementary models is exceptionally good except at large reaction times.

Correlation coefficients between these two global parameters and the rate constants of the elementary mechanism are listed in Table II. Recall that the elementary model consisted of 54 rate parameters; only those which had a significant influence on the global parameter values (i.e., $> 0.1 \times \partial \ln \beta_i / \partial \ln \alpha_j |_{\text{max}}$) are listed in Table II (and future tables). Table II

reveals that both A_{ov} and E_{ov} are correlated to many of the same and also to several different elementary reactions. This latter fact would normally not be perceived since A_{ov} and E_{ov} are strongly coupled to each other in the global model (as determined by the elementary sensitivities). Specifically, both A_{ov} and E_{ov} are highly correlated to the rate constant for the reaction between CO and hydroxyl radical. The overall activation energy is also highly coupled to the equilibrium constants of the two chain branching reactions,



It should therefore not be surprising that the value of E_{ov} closely resembles the activation energies of the two reactions above, especially since the activation energy for the rate constant, k_{CO+OH} , in this temperature range is small ($\approx 6 \text{ kcal/mol}$).

In contrast, the overall frequency factor is sensitive to the rate constants of $H + O_2 + M$ and $CO_2 + H$. The importance of this latter reaction on A_{ov} may be responsible for some of the discrepancy between the global model and elementary model at large reaction times. The one-step mechanism was originally based on only the forward step of $CO + OH$ and consequently no allowance was made for equilibration. Table II clearly shows that the reverse step becomes important at these high temperatures. As reaction times increase and/or the reaction temperature is raised, this reverse step will inevitably play a more dominant role. Recent global models²⁰ have added a second reaction, $CO_2 \rightarrow CO + \frac{1}{2} O_2$, to account for this event.

The importance of the $H + O_2 + M \rightarrow HO_2 + M$ reaction at these temperatures is surprising, but may be related to the fact that the $H + O_2 \rightarrow OH + H$ reaction is nearly equilibrated. In fact, this reaction has a small net rate of progress in the reverse direction allowing the three body reaction to compete favorably.

Note also from Table II that for some reactions of the elementary model,

the resulting correlation with the two global parameters affects the overall kinetics in an opposite sense. For example, an increase in rate constant $k_{\text{OH}+\text{CO}}$ correlates to a decrease in A_{ov} and E_{ov} . A decrease in E_{ov} increases the overall rate of CO disappearance, whereas a decrease in A_{ov} , decreases this rate. However, the net effect as determined by $\partial \ln k_{\text{ov}} / \partial \ln k_{\text{CO}+\text{OH}}$ is an increase. Moreover, these results suggest that there may be situations where both A_{ov} and E_{ov} are highly coupled to a particular elementary reaction, but their net effect on the overall kinetics may be zero. Information such as this can be valuable for guidance towards improving the present model.

In Table III, the induction time parameters, B and F, and the associated correlation coefficients are reported. The reactions most correlated to B are $\text{CO} + \text{OH}$ and $\text{CO} + \text{O}_2$ and to F the reaction $\text{O} + \text{H}_2\text{O}$. Note for τ , when $\partial \ln B / \partial \ln k_j$ and $\partial \ln F / \partial \ln k_j$ have the same senses, they each affect τ in the same manner. Consequently, it can be seen from Table III that at a temperature of 2000 K, the overall effect of a perturbation in the rate constant $k_{\text{H}+\text{O}_2+\text{M}}$ on τ is nearly zero, whereas at a temperature of 1600 K, the net effect of a perturbation in $k_{\text{H}+\text{O}_2+\text{M}}$ is to lengthen the induction time.

The results of A_{ov} , E_{ov} , $\partial \ln A_{\text{ov}} / \partial \ln k_j$, and $\partial \ln E_{\text{ov}} / \partial \ln k_j$ for the intermediate and low temperature ranges are tabulated in Tables IV and V, respectively. Examination of these tables immediately reveals a significant change in the elementary structure. These changes appear in the global model as variations in the global parameters.

In the intermediate temperature regime, both the values of A_{ov} and E_{ov} increase relative to their values in the high temperature regime. The controlling elementary processes are $\text{H} + \text{O}_2$ and $\text{H} + \text{O}_2 + \text{M}$ followed by $\text{CO} + \text{OH}$. Note that the reverse reactions of the branching reactions are not as important as in the high temperature regime, and that the reaction of $\text{CO}_2 + \text{H}$ is not important at all.

In the low temperature regime, A_{ov} and E_{ov} decrease relative to the intermediate temperature regime values, but remain larger than their values in the high temperature regime. In this temperature range, it is evident that $H + O_2 + M$ remains competitive with $H + O_2$ for H-atoms, and $CO + O + M$ competes with $O + H_2O$ for O-atoms. More importantly, the reaction of CO with HO_2 now affects A_{ov} and E_{ov} and dominates over the importance of $CO + OH$.

Considering the entire temperature range, the behavior of k_{ov} may now be explained by the results of the correlation coefficients. Starting in the intermediate zone, extrapolation of this rate constant into the high temperature zone overpredicts the actual value. This apparent decrease results from the partial equilibration of several steps, particularly the $CO + OH = CO_2 + H$ reaction, and the increased importance of radical - radical reactions. In extrapolating k_{ov} from the intermediate regime to the low temperature regime, we find k_{ov} to be under-predicted. Here the additional reaction of CO with HO_2 (and with O-atoms) increases k_{ov} . The peak in the overall activation energy in the intermediate temperature regime is indicative of a system changing from one of marginal stability in the low temperature regime (high E_{ov}) to one of greater stability in the high temperature regime (low E_{ov}).

GLOBAL MODEL DEVELOPMENT

If the variations in the global parameters are to be eliminated from the current model, it is clear that the functional form of k_{ov} and τ must be altered. As mentioned earlier, one advantage of having available an elementary model was that it could be used to generate the global model itself. The mathematical techniques necessary for such a process have been and continue to be topics of much needed research. The non-linearity in combustion kinetics equations make this a particularly difficult task. However, several related techniques currently exist, and to emphasize their diversity and complexity, a few examples are listed below.

(i) Missing Components Analysis - In this analysis, additional parameters are added to the existing functional relationship. The feature sensitivity coefficients are evaluated with the newly defined parameters preset at null values. The resulting magnitudes of these coefficients indicate the importance of these new parameters in the altered functional relationship. The method involves a trial and error approach, and although ultimately one must actually add the new components to test their effects, some valuable guidance can be obtained from the missing model sensitivity coefficients.

(ii) The correlated behavioral traits of the Green's function matrix can serve as a lumping reduction diagnostic tool for choosing lumping parameters to which the outputs of interest respond similarly. The Green's function of Eq. (3) is a generalized memory function which measures the stability of the i -th observable at time t and position x with respect to variations of the j -th observable at prior time t' and position x' . For a temporal system, the elements of \underline{G} take the form $\partial O_i(t)/\partial O_j(t')$, $t \geq t'$. To illustrate the potential application of these gradients, Fig. 5 is a schematic diagram of all the response functions obtained from the elementary model for a dilute mixture reacting at 1100 K and 1 atm. In the figure, the complex response surfaces are represented by symbols; all elements represented by the same symbol have similarly behaved response surfaces. Those with the same shape, but shaded in, are of opposite sign. Blank spaces indicate a response surface which could not be closely matched with another. These results suggest that one "effective" radical could supplant all others since they have the same response characteristics with regard to the major species. In premixed flame calculations, the corresponding matrix indicates that two radicals are required, a low temperature radical and a high temperature radical.

The rank of the Green's function matrix and its eigenvalue - eigenvector analysis can be useful for such lumping. For example, if the rank of \underline{G} is

less than its dimension, then there is a corresponding reduced number of independent species implied. In practice, this issue could be addressed by a rank reduction to some specified acceptable numerical tolerance. Furthermore, the eigenvalues of \underline{G} contain valuable information regarding the natural time scales (stability) of the system. For lumping concerns, this information may be used to eliminate the portion of the system responsible for short time transient behavior. The remaining portion of the system would then be identified by the corresponding long time scale eigenvector of \underline{G} . If short time behavior was of concern, the opposite elimination could be done.

Other recent mathematical techniques which could be beneficial to model lumping include the Lie algebra approach²⁴ and the singular perturbation procedure.²⁵

CONCLUDING REMARKS

This paper has shown the commonly used one-step mechanism for moist CO oxidation to exhibit numerous complexities in its behavior over the physical parameter ranges of importance to combustion kinetics. Furthermore, global models found valid for one physical system were found generally not valid for another. Correlation coefficients, which relate the fundamental parameters between two chemical kinetic models (global and elementary), were derived and used to identify which elementary reactions control the values of the global parameters. This information was used to explain the complex dependence of k_{ov} on T . Work in the future should be directed toward the development and application of systematic mathematical techniques, such as those introduced in the previous section along with the correlation coefficients presented here, to obtain a better, universal model for moist CO oxidation.

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TABLE I. OVERALL RATE PARAMETERS FOR MOIST CO OXIDATION*

Reference	T (K)	A_{ov}^1	E_{ov}^2	a	b	c
Friedman & Cyphers [1]	2010	$5.3(9)^3$	20	1	0.5	0
Hottel et al. [23]	1280 - 1535	1.2(11)	16	1	0.5	0.3
Lavrov [22]	1063 - 1593	1.8(12)	28.3	1	0.5	0.25
Dryer & Glassman [21]	1050 - 1200	3.9(14)	40	1	0.5	0.25
Lyon et al. [2]	1123 - 1298	1.5(10)	23.6	1	0.5	0.25

* $-d[CO]/dt = A_{ov} \exp(-E_{ov}/RT) [CO]^a [H_2O]^b [O_2]^c$

¹ $(cm^3 mol^{-1})^{3/4} s^{-1}$

² kcal/mol

³ numbers in parentheses denote powers of ten.

TABLE II. CORRELATIONS BETWEEN GLOBAL AND ELEMENTARY KINETIC
PARAMETERS AT HIGH TEMPERATURES (1600 - 2100 K)

$$A_{ov} = 1.06 \times 10^{11} (\text{cm}^3 \text{mol}^{-1})^{3/4} \text{s}^{-1}$$

$$E_{ov} = 21 \text{ kcal/mol}$$

Reaction	$\partial \ln A_{ov} / \partial \ln k_j$
$\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H}$	-0.208
$\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M}$	-0.056
$\text{O} + \text{H}_2\text{O} \rightarrow \text{OH} + \text{OH}$	-0.051
$\text{CO}_2 + \text{H} \rightarrow \text{CO} + \text{OH}$	0.037
$\text{CO} + \text{O}_2 \rightarrow \text{CO}_2 + \text{O}$	-0.037
$\text{OH} + \text{OH} \rightarrow \text{O} + \text{H}_2\text{O}$	0.035
$\text{OH} + \text{O} \rightarrow \text{H} + \text{O}_2$	0.021
$\text{HO}_2 + \text{O} \rightarrow \text{O}_2 + \text{OH}$	0.019
$\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}$	-0.017
Reaction	$\partial \ln E_{ov} / \partial \ln k_j$
$\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H}$	-0.309
$\text{O} + \text{H}_2\text{O} \rightarrow \text{OH} + \text{OH}$	-0.086
$\text{OH} + \text{OH} \rightarrow \text{O} + \text{H}_2\text{O}$	0.063
$\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}$	-0.039
$\text{OH} + \text{O} \rightarrow \text{H} + \text{O}_2$	0.035
$\text{HO}_2 + \text{O} \rightarrow \text{O}_2 + \text{OH}$	0.019
$\text{CO} + \text{O}_2 \rightarrow \text{CO}_2 + \text{O}$	0.019
$\text{CO}_2 + \text{H} \rightarrow \text{CO} + \text{OH}$	0.013

TABLE III. CORRELATIONS BETWEEN GLOBAL AND ELEMENTARY KINETIC
PARAMETERS DURING THE INDUCTION TIME AT HIGH TEMPERATURES

$$B = 9.30 \times 10^{-35} \text{ (cm}^3/\text{molec)}^{1.75} \text{ s} = 3.83 \times 10^7 \text{ (cm}^3/\text{mol)}^{1.75} \text{ s}$$

$$F = 7.98 \text{ kcal/mol}$$

Induction Time (s)	System 1	System 2	System 3
τ^d	1.423×10^{-4}	2.168×10^{-4}	3.476×10^{-4}
τ^g	1.423×10^{-4}	2.139×10^{-4}	3.474×10^{-4}

Reaction	$\partial \ln B / \partial \ln k_j$
$\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H}$	-0.456
$\text{CO} + \text{O}_2 \rightarrow \text{CO}_2 + \text{O}$	-0.245
$\text{H}_2\text{O} + \text{O}_2 \rightarrow \text{HO}_2 + \text{OH}$	-0.072
$\text{O} + \text{H}_2\text{O} \rightarrow \text{OH} + \text{OH}$	0.053
$\text{OH} + \text{OH} \rightarrow \text{O} + \text{H}_2\text{O}$	0.048
$\text{H}_2\text{O} + \text{M} \rightarrow \text{H} + \text{OH} + \text{M}$	-0.035
$\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M}$	-0.026
$\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}$	0.024

Reaction	$\partial \ln F / \partial \ln k_j$
$\text{O} + \text{H}_2\text{O} \rightarrow \text{OH} + \text{OH}$	-0.143
$\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H}$	-0.072
$\text{CO} + \text{O}_2 \rightarrow \text{CO}_2 + \text{O}$	0.044
$\text{H}_2\text{O} + \text{O}_2 \rightarrow \text{HO}_2 + \text{OH}$	0.026
$\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}$	-0.021
$\text{H}_2\text{O} + \text{M} \rightarrow \text{H} + \text{OH} + \text{M}$	0.014
$\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M}$	0.013

TABLE IV. CORRELATIONS BETWEEN GLOBAL AND ELEMENTARY KINETIC
PARAMETERS AT INTERMEDIATE TEMPERATURES (900 - 1000 K)

$$A_{ov} = 7.20 \times 10^{20} (\text{cm}^3 \text{mol}^{-1})^{3/4} \text{s}^{-1}$$

$$E_{ov} = 69 \text{ kcal/mol}$$

Reaction	$\partial \ln A_{ov} / \partial \ln k_j$
$\text{H}_2\text{O}_2 + \text{M} \rightarrow \text{OH} + \text{OH} + \text{M}$	1.080
$\text{H}_2\text{O}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{HO}_2$	-0.802
$\text{OH} + \text{O} \rightarrow \text{H} + \text{O}_2$	0.753
$\text{CO} + \text{O} + \text{M} \rightarrow \text{CO}_2 + \text{M}$	-0.696
$\text{O} + \text{H}_2\text{O} \rightarrow \text{OH} + \text{OH}$	0.687
$\text{HO}_2 + \text{O} \rightarrow \text{O}_2 + \text{OH}$	0.664
$\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$	0.456
$\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M}$	0.357
$\text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$	0.286
$\text{CO} + \text{HO}_2 \rightarrow \text{CO}_2 + \text{OH}$	0.274
$\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H}$	-0.164
$\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}$	-0.152
Reaction	$\partial \ln E_{ov} / \partial \ln k_j$
$\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M}$	0.0639
$\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}$	-0.0579
$\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H}$	-0.0352
$\text{OH} + \text{O} \rightarrow \text{H} + \text{O}_2$	0.0262
$\text{H}_2\text{O}_2 + \text{M} \rightarrow \text{OH} + \text{OH} + \text{M}$	0.0187
$\text{H}_2\text{O}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{HO}_2$	-0.0131
$\text{HO}_2 + \text{O} \rightarrow \text{O}_2 + \text{OH}$	-0.0128

TABLE V. CORRELATIONS BETWEEN GLOBAL AND ELEMENTARY KINETIC
PARAMETERS AT LOW TEMPERATURES (650 - 750 K)

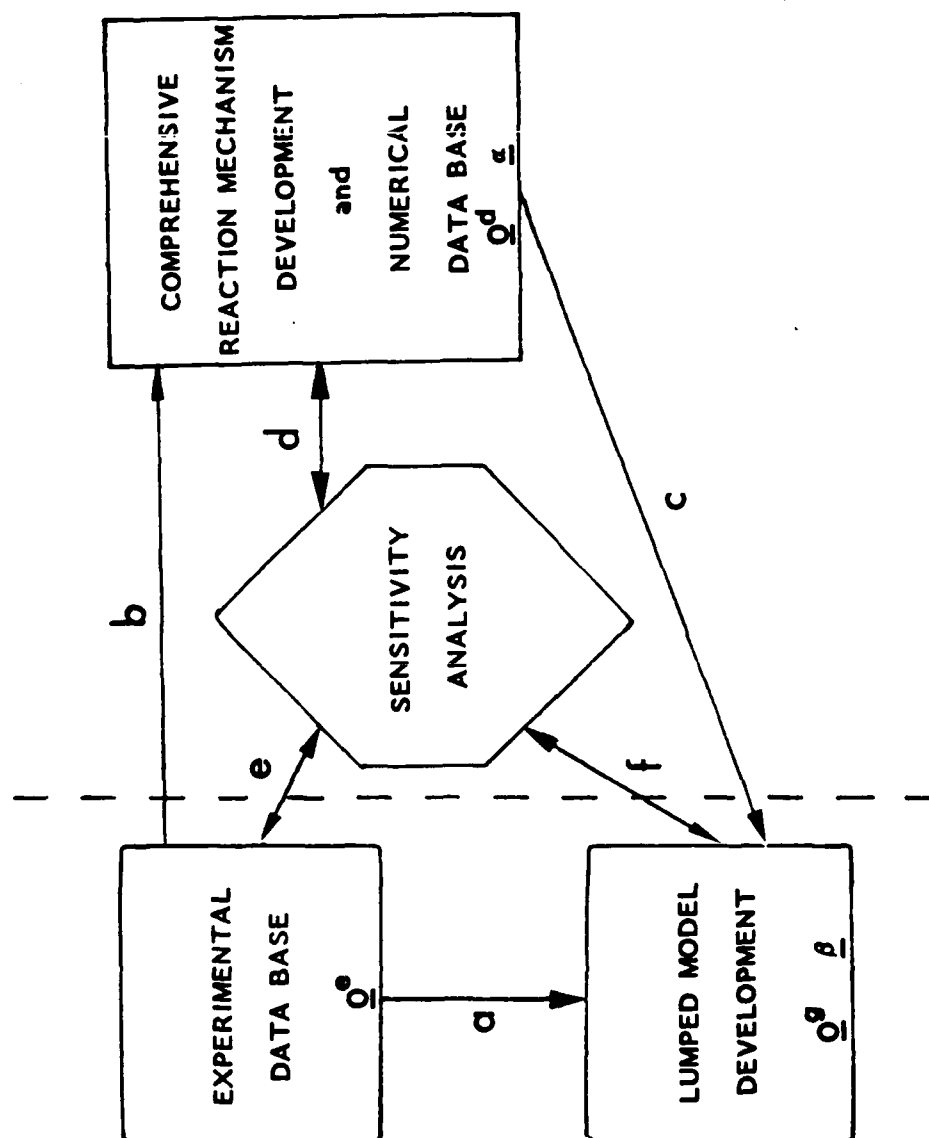
$$A_{\text{ov}} = 5.80 \times 10^{14} (\text{cm}^3 \text{mol}^{-1})^{3/4} \text{s}^{-1}$$

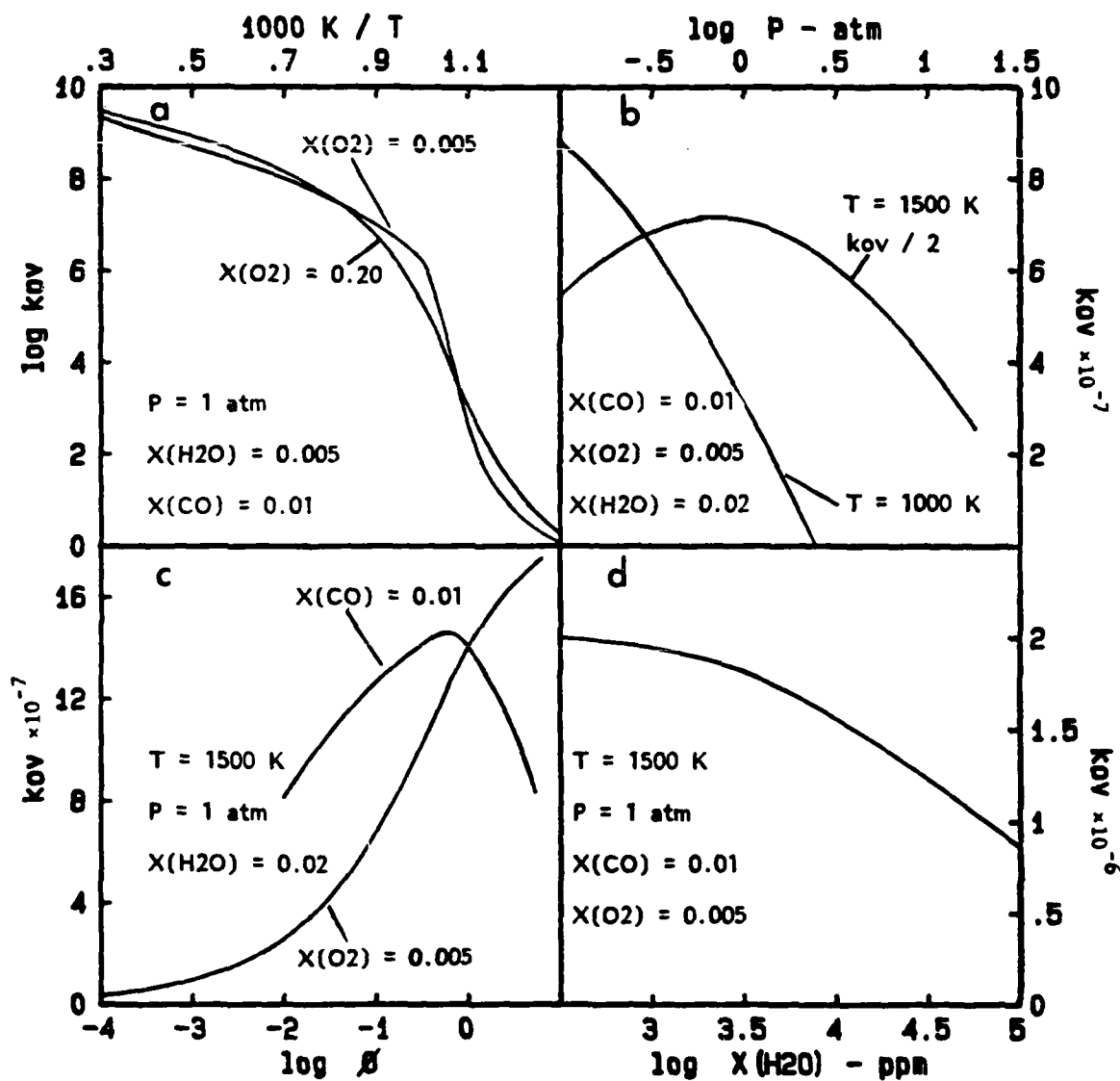
$$E_{\text{ov}} = 56 \text{ kcal/mol}$$

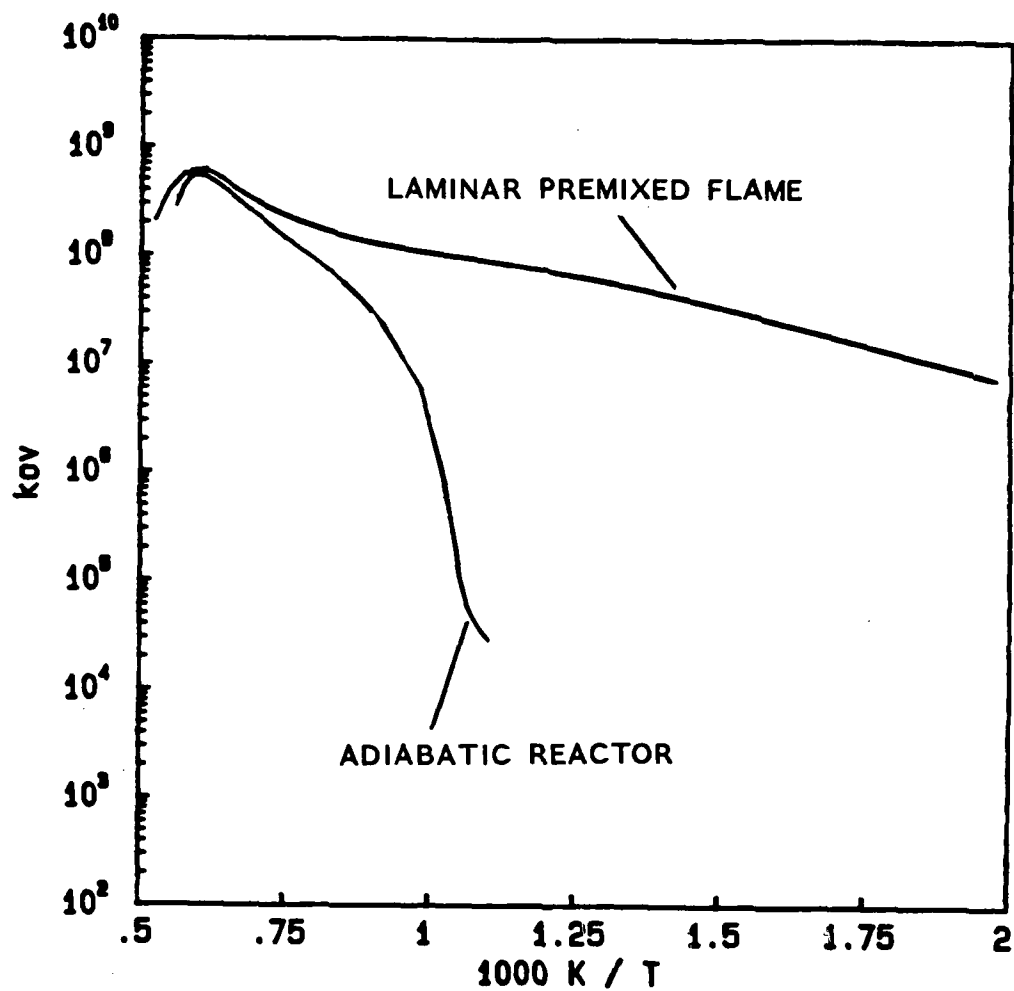
Reaction	$\partial \ln A_{\text{ov}} / \partial \ln k_j$	$\partial \ln E_{\text{ov}} / \partial \ln k_j$
$\text{O} + \text{CO} + \text{M} \rightarrow \text{CO}_2 + \text{M}$	-10.49	-0.250
$\text{O} + \text{H}_2\text{O} \rightarrow \text{OH} + \text{OH}$	10.48	0.250
$\text{CO} + \text{HO}_2 \rightarrow \text{CO}_2 + \text{OH}$	10.24	0.244
$\text{CO} + \text{O}_2 \rightarrow \text{CO}_2 + \text{O}$	3.06	0.049
$\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M}$	-1.57	-0.038
$\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}$	1.56	0.037
$\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H}$	-1.01	-0.024

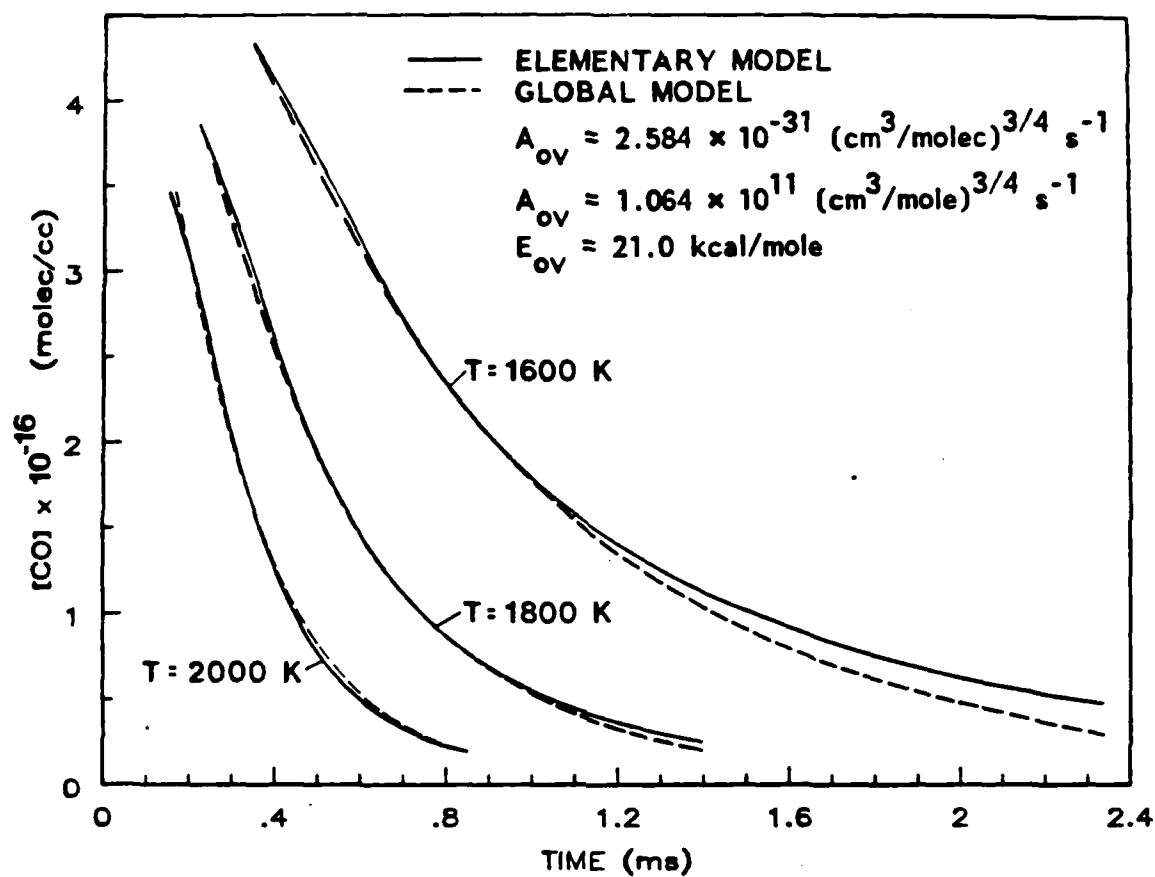
Figure Captions






















































































1. Schematic diagram of a generalized approach to global modeling illustrating the connections between experiment, detailed kinetic model development, global model development, and sensitivity analysis theory.
2. (a) The overall rate constant, k_{ov} , for a temporal CO/H₂O/O₂ kinetic system determined from numerical calculation data. For all plots, the units of k_{ov} are (cm³/mol)^{3/4}/s. Here, $\log k_{ov} = \log(d[CO_2]/dt) - \log[CO] - 0.5\log[H_2O] - 0.25\log[O_2]$. To obtain plot, several isothermal calculations were run at different initial temperatures. Note the non-Arrhenius behavior of k_{ov} . At a temperature of approximately 940 K, the system crosses the explosion peninsula of 1 atm. (b) The overall rate constant for a temporal CO/H₂O/O₂ kinetic system for various pressures at 1000 K and 1500 K. The decrease in k_{ov} at high pressure (1000 K) indicates the onset of slow CO reaction. (c) Variation in k_{ov} for the isothermal CO/H₂O/O₂ system for various equivalence ratios at 1500 K and 1 atm. For one curve, ϕ is varied by changing the initial CO concentration. The decrease in k_{ov} with decreasing $[CO(t=0)]$ is proportional to the decrease in the OH radical concentration overshoot. At very lean equivalence ratios, k_{ov} asymptotically approaches a value determined by the equilibrium OH concentration. For the other curve, ϕ is varied by changing the initial O₂ concentration. The decrease in k_{ov} at lean mixtures is surprising and is a good example where the sensitivity analysis techniques described could be beneficial. (d) Variation in k_{ov} for the temporal CO/H₂O/O₂ system for various water vapor concentrations.
3. Comparison of the overall rate constant obtained from a laminar premixed flame and from an adiabatic flow reactor. The units of k_{ov} are (cm³/mol)^{3/4}/s. The initial temperature for the flame is 298 K and for the adiabatic flow reactor, 835 K. The latter temperature was used to initiate the reaction. Both systems are at atmospheric pressure. The initial composition for both systems is; $X(CO) = 0.515$, $X(O_2) = 0.0987$, $X(H_2O) = 0.0072$, $X(H_2) = 0.0079$, and $X(N_2) = 0.371$. The large discrepancies at low and high temperatures are due to the influence of diffusion on the chemistry.
4. Comparisons of the CO concentration profile from global and elementary models. The global calculations were obtained with lumped parameters of $A_{ov} = 1.064 \times 10^{11}$ (cm³/mol)^{3/4}/s and $E_{ov} = 21.0$ kcal/mol. Initial conditions of the three runs are: $P = 1$ atm, $X(CO) = 0.01$, $X(O_2) = 0.20$, $X(H_2O) = 0.01$, $X(N_2) = 0.78$, (1) $T = 2000$ K, (2) $T = 1800$ K, and (3) $T = 1600$ K.
5. Schematic diagram of the moist CO oxidation response function, $\partial O_i(t)/\partial O_j(t')$, $t \geq t'$. This gradient is an element of the Green's function matrix, $G_{ij}(t, t')$ and is a generalized memory function which measures the stability of the i -th observable at time t with respect to variations of the j -th observable at prior time t' . In the figure, elements of similar shape have similarly behaved response surfaces as a function of t and t' . Those with the same shape, but shaded in, are of opposite sign. Blank spaces indicate a response surface which could not be closely matched with another. Initial conditions of the reacting mixture are: $P = 1$ atm, $T = 1100$ K, $X(CO) = 0.002$, $X(O_2) = 0.028$, $X(H_2O) = 0.01$, and $X(N_2) = 0.96$.









$t' \backslash t$	CO ₂	CO	O ₂	H ₂ O	H ₂	HCO	H	HO ₂	H ₂ O ₂	O	OH
CO ₂											
CO											
O ₂											
H ₂ O											
H ₂											
HCO											
H											
HO ₂											
H ₂ O ₂											
O											
OH	